Chemistry Spectrum

AUGUST 2016 ₹30

REGULARS
CHEMISTRY @ SPECTRUM FOR YOU
DO YOU KNOW
PERSONALITIES SPECTRUM
BRAIN TEASERS

MOTIVATOR'S SPECTRUM

GAURAV DIDWANIA
JEE AIR 9th RANK

ANINESH BOHARA
JEE AIR 19th RANK

METICULOUS ANALYSIS

NUCLEOPHILIC SUBSTITUTION
A Bird's Eyeview

CHEMISTRY CONCENTRATE
ELECTROCHEMISTRY IN CONNECTION WITH REDOX

EQUILIBRIA: A FREE ENERGY PERCEPTION

EXPLICATION
ELEMENTS HOW THEY WERE DISCOVERED

CONCEPT MAP
ATOMIC STRUCTURE

JEE ADVANCED DRILL
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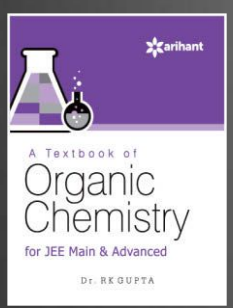

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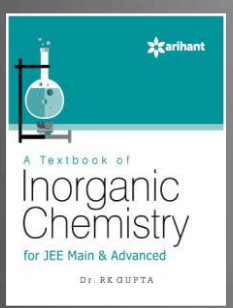

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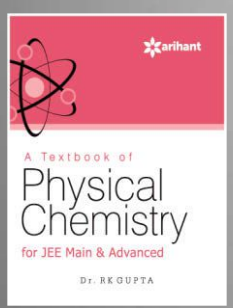

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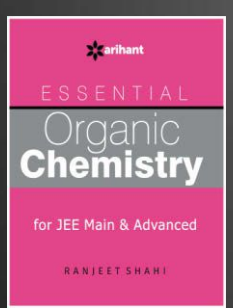

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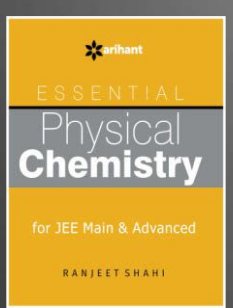

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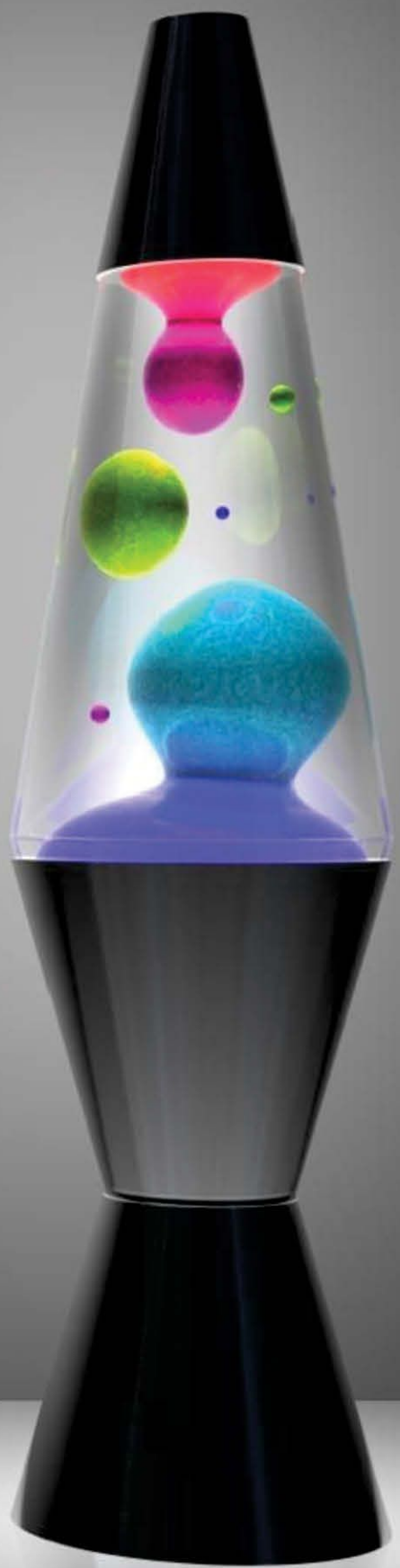

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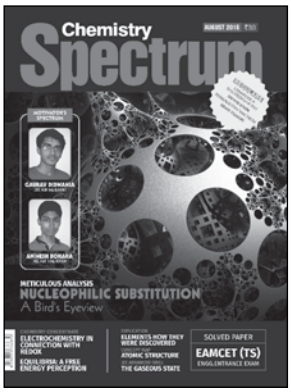

Dear Aspirants,

By now your studies would be in full swing after such a valuable summer break. The spectrum seed which was sown few years back is also taking shape of a tree, gradually with multiple branches. The overwhelming response given by you plays a vital role in its growth.

Chemistry is very vast and proved very useful in sorting many of our problems. The beautiful colours, that seen in the plant world, are the result of the presence of organic compounds that absorb certain wavelengths of visible light and reflect the rest. Everything in our surroundings can have its explanation in Chemistry. Molecules are formed in the cool region of space when individual atoms or ions happen to collide and make bonding with each other. These are not seen in stars as the bonds would not survive in the high temperatures of stars. Even the shells of atoms retain their electrons at such huge temperatures. It simply indicates that in stars the matter exists as plasma of ionized atoms and unbound electrons. Over 100 different molecules have been identified by the astronomers in the dense molecular clouds like Orian Nebula. These molecular clouds are dense only by astronomical standards even the densest clouds are about 100 billion times lighter and thinner than the earth's atmosphere. Thus, we can say that not even the chemistry around us but the chemistry far away from us is also very complicated and Mysterious. **Einstein** in following lines truly described the beauty of Mysterious as

"The most beautiful thing we can experience is the MYSTERIOUS.
It is the source of all true art and science"

We are trying hard to provide more and more material for your practice within the purview of our limitations. Hope you all are also trying best to Crack the hard nut called EXAMINATION. The spectrum team will be anxiously waiting for your feed backs and comments.

Good luck

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JEE TOPPER

GAURAV DIDWANIA

AIR 9th RANK

Q Achieving top position was a surprise for you or you were expecting it?
Gaurav- It was a surprise for me , I was expecting a rank around 50 but coming at No. 3 is really a pleasant surprise .

Q Please share your feelings after achieving such a mile stone?
Gaurav- Feeling too good and very confident.

Q In how many attempts did you get this success?
Gaurav- Ist attempt.

Q How did you manage to prepare for board examinations and competitive exams simultaneously?
Gaurav- Started preparing for JEE from 11th class and started preparing for Board exams from Feb. last.

Q What were your subject wise score in .....(exam name) and 12th boards?
Gaurav- 90 %.

Q Please share the secret of your success with our readers .
Gaurav- One should have a good friend circle and there should not be any pressure from parents.

Q Tell us something about your source of inspiration.
Gaurav- Inspired by my maternal Uncle Mr. Devesh Aggarwal who is an engineer .

MESSAGE TO FUTURE ASPIRANTS

Trust your teacher, don't get confused by other things, consult your teacher for books, have good friend circle, don't put pressure on yourself and avoid stress, always focus on your ultimate goal.

Q What was your study plan; please explain in details so that our readers can also follow it?
Gaurav- I did not follow any time table. My Physics was strong so given maximum focus on Maths and Chemistry .

Q Did your Study Plan remain same throughout the year; at the start of the session, after completion of syllabus and just 1-2 months before the exam or you had different plans for different phases?
Gaurav- I have started the preparation for JEE in 11th and use to study for Boards and JEE together .

Q How many hours of study, is sufficient for such a success?
Gaurav- A regular study of 6 to 7 hours is required .

Q Tell us something about your study techniques like How do you memorise the facts, how did you have your revision and how you assessed your preparation from time to time.
Gaurav- Repeat and revise the topics again and again and you will learn everything.

Q Tell us about your family and the role of your family members in guiding you towards this spectacular performance in the exam?
Gaurav- My Parents help in boosting my confidence , they always motivated me a, there was no pressure from their side.

Q Share something about the Weak and Strong points of your personality.
Gaurav- I use to perform very good in challenging environment .

Q Did you devote equal time to all the subjects or more weightage or one or two subjects as compared to other subjects?
Gaurav- Equal weightage to Every subject and topic

Q Were there any weak areas of yours in any subject(s)? How did you cope up with those?
Gaurav- Complex numbers im Maths and practiced it again and again.

Q How your teachers/ Mentors helped in achieving this goal?
Gaurav- Teachers/ Mentors always motivated me , they were always available to help me , I have full trust on them.

Q Which is your dream institution and which stream do you wish to pursue?
Gaurav- IIT Mumbai , Computer Science .

Q Besides studies, what do you do, i.e. what are your hobbies and how you match up with these hobbies during your studies? What you do during the breaks from your studies?
Gaurav- CRICKET and Seeing Movies .

Q Now-a-days Social Media like Facebook, Twitter etc; is a big trend? Do you also engage with these, does it affect the studies? Please give some advice to our readers.
Gaurav- I used Whatsapp for discussing questions and problems among friend circle .

Q Did you find Arihant books helping you to get this success?
Gaurav- Studied Understanding Physics by D C Pandey and it helped me in understanding the topics of Physics.

JEE TOPPER

ANINESH BOHARA

AIR 19th RANK

Q Achieving top position was a surprise for you or you were expecting it?
Aninesh- On the basis of my preparation in the past few years I was expecting a top 50 rank but rank 19 surely come as a surprise for me.

Q Please share your feelings after achieving such a mile stone?
Aninesh- I feel vary good to achieve such a milestone and I would like to dedicate this success to my family & the faculty of Fiit-jee

Q In how many attempts did you get this success? _____
Aninesh- 1st attempt.

Q How did you manage to prepare for board examinations and competitive exams simultaneously?
Aninesh- I generally, focused on competitive exam preparation, board was covered simultaneously as the concepts are same for both of them.

Q Please share the secret of your success with our readers.
Aninesh- I studied only when I had full concentration and full usage to study. I feel that quality and time matter not the quantity and time.

Q Tell us something about your source of inspiration.
Aninesh- I was inspired by my father in childhood, who himself a engineer, which cause my interest in science and mathematics.

SCORE CARD

Board: Physics 97%, Chemistry 99%, Biology 100%, Mathematics 99%, English 77%,Engineering Graphics 99%

JEE Main: 310 marks, **JEE Advance** 281 marks

MESSAGE TO FUTURE ASPIRANTS

Always have confidence in yourself and don't take undue pressure as these are just another hurdle in life

Q What was your study plan; please explain in details so that our readers can also follow it?

Aninesh- I generally did not follow some fixed time table.

Q Did your study plan remain same throughout the year; at the start of the session, after completion of syllabus and just 1-2 months before the exam or you had different plans for different phases?

Q How many hours of study, is sufficient for such a success?

Aninesh- 6-10 h is sufficient for such a success.

Q Tell us something about your study techniques like. How do you memorise the facts, how did you have your revision and how you assessed your preparation from time to time.

Aninesh- Go through the note from time to time.

Q Tell us about your family and the role of your family members in guiding you towards this spectacular performance in the exam?

Aninesh- Motivation from whole family.

Q Share something about the Weak & Strong points of your personality.

Aninesh- Chemistry is my weak point & Maths is my strong point.

Q Did you devote equal time to all the subjects or more weightage or one or two subjects as compared to other subjects

Aninesh- I devote more time on Chemistry because its my weak point.

Q Were there any weak areas of yours in any subject(s)? How did you cope up with those?

Q How your teachers/mentors helped in achieving this goal?

Aninesh- Fiit-jee (Punjabibagh center) Phy- Anil Kr.Seth ,Math- Sanjay Verma,
Chem- Vikram Singh.
KIIT World School Pritampura-Former Principal Sangeeta Bhatia.

Q Which is your dream institution and which stream do you wish to pursue?

Aninesh- Institue-IIT Bombay Stream- Computer Science(CSE).

Q Besides studies, what do you do, i.e. what are your hobbies and how you match up with these hobbies during your studies? What you do during the breaks from your studies?

Aninesh- Playing small or Light Mobile games.

Q Nowadays Social Media like Facebook, Twitter etc; is a big trend? Do you also engage with these, does it affect the studies? Please give some advice to our readers.

Aninesh- Almost closed.

Q Please tell us the about the books and other reference material that ensured your success?

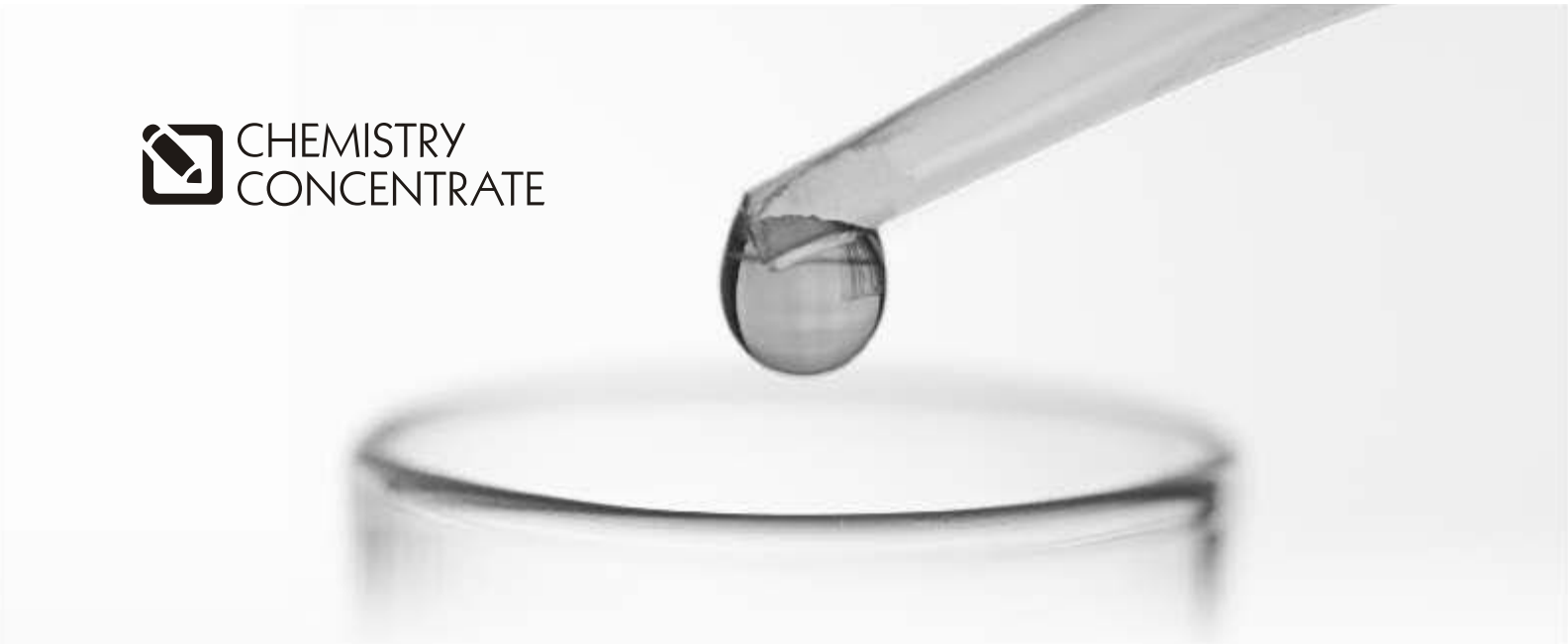
Aninesh- Physics-DC Pandye
Math-Amit M Aggrwal.

Q Did you find Arihant books helping you to get this success?

Aninesh- CBSE Chaperwise for board examination
38 years papers for IIT examination.

Q How spectrum was helpful in your studies?

Aninesh- Chemistry spectrum was helpful for me for my preparation.



ELECTROCHEMISTRY IN CONNECTION WITH REDOX

Electrochemistry is a branch of chemistry that deals with interconversion of chemical energy and electrical energy. Redox reactions involve the transfer of electrons from one species to another. Electrochemistry is the study of electron flow within redox reactions, i.e. the relationship between electricity and chemical changes. Electrochemical reactions are used on a larger scale in the industrial manufacture of some metals and other widely used substances like chlorine, by electrolysis. In this article, we shall read how electrochemisty and redox reactions are connected to each other.

(I) Oxidation and Reduction

The term **oxidation** was first used for those chemical reactions in which oxygen is added to an element or a compound. The reverse of such a process is defined as **reduction**. Both the above written terms can be defined in many ways as.

	Oxidation		Reduction
(i)	Addition of oxygen or electronegative element.	(i)	Removal of oxygen or electronegative element.
(ii)	Removal of hydrogen or electropositive element.	(ii)	Addition of hydrogen or electropositive element.
(iii)	Loss of electron(s).	(iii)	Gain of electron(s).

(II) Oxidising and Reducing Agents

Oxidising agents or **oxidants** are those substances which themselves gets reduced and oxidise the other species.

Reducing agents or **reductant** are those substances which themselves gets oxidised and reduce the other species.

REMEMBER

- Molecules consisting of highly electronegative elements like oxygen (O), halogen (*X*) etc; are good oxidising agents.
- The molecules in which an atom shows high oxidation state like $K\underline{Cl}O_3$, $\underline{Fe}Cl_3$, $K\underline{Mn}O_4$, $H\underline{N}O_3$ etc. can get reduced easily.
- Metal oxides, e.g. CaO, MgO, SO_3. etc., are good oxidising agents.
- All the metals are good reducing agents, e.g. Na, Al etc.
- The compounds having elements in their lower oxidation state like– $PtCl_2$, can get oxidised easily.
- Some non-metals (C, S, P etc), halogen acids (HI, HCl), metal hydrides (NaH, LiH etc.) also act as reducing agents.

(III) Oxidation Number

Oxidation number of an element, in a particular compound, is equal to the number of electrons lost, gained or shared by that element. It is positive when electrons are lost and negative when electrons are gained.

Some Common Oxidation states

Group	Common oxidations states except zero in free states
Alkali metals	+1
Alkaline earth metals	+2
Boron family	+ 3, + 1
Carbon family	+ 4, + 3, +2 +1, –1, – 2, – 3, – 4
Nitrogen family	+ 5, + 3, + 1, – 1, – 3
Oxygen family	+ 6, + 4, + 2, – 2
Halogens	+ 7, + 5, + 3, + 1, – 1
Zero group	Zero

Note The oxidation number of hydrogen is + 1 when combined with non-metals and – 1 when combined with active metals.

Identifying Oxidising and Reducing Agents

Consider the redox reaction between zinc metal and copper (II) ions. The net ionic equation is

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

To see more clearly how electrons are transferred, the above overall reaction can be written into two simultaneous half-reactions, i.e. oxidation half-reaction and reduction half-reaction.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \quad ...(i)$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad ...(ii)$$

- By writing the oxidation number of each element above or below the equation we can see how the oxidation number change.
- The oxidation number of Zn changes from 0 to +2 and that of Cu changes from +2 to 0. Thus, this is an oxidation-reduction reaction.
- Zn acts as reducing agent as it itself get oxidised and help in reducing copper while Cu acts as an oxidising agent because it itself get reduced and help in oxidising Zn.

Example 1 Which quantities are conserved in all oxidation reduction reactions?

(a) Only charge *(b)* Only mass
(c) Both charge and mass *(d)* Neither charge nor mass

Sol. ***(c)*** Oxidation involves loss of electrons and reduction involves gain of electrons, hence in case of oxidation-reduction reaction charge remains conserved. Moreover, in all chemical reactions mass also remains conserved.

e.g. $H^+ + H_2O + NO_3^- + H_2S \longrightarrow NH_4^+ + HSO_4^-$

Charge: $+1 + 0 + (-1) + 0 = +1 + (-1) = 0$

Mass: $1 + 18 + (14 + 48) + (32 + 2) = (14 + 4) + (1 + 32 + 64)$

$115 = 115$

Example 2 Which is the best description of the behaviour of bromine in the reaction given below?

$$H_2O + Br_2 \longrightarrow HOBr + HBr$$

(a) Only reduced *(b)* Only proton acceptor
(c) Only oxidised *(d)* Both (a) and (c)

Sol. ***(d)***

$H_2O + Br_2 \longrightarrow HOBr + HBr$

HOBr: Electronegative element; HBr: Electronegative element

Since, in this reaction, addition of electronegative as well as addition of electropositive element is seen with Br. Thus, bromine is oxidised as well as reduced.

Example 3 In the reaction,

$$4P + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$$

(a) P is only oxidised
(b) P is only reduced
(c) P is both oxidised as well as reduced
(d) None of the above

Sol. ***(c)***

$$\overset{0}{4P} + 3KOH + 3H_2O \longrightarrow \overset{+1}{3KH_2PO_2} + \overset{-3}{PH_3}$$

+1 unit increase; – 3 unit decrease

Hence, P is both oxidised as well as reduced.

Example 4 In the reaction,

$$H_2O_2 + Na_2CO_3 \longrightarrow Na_2O_2 + CO_2 + H_2O$$

the substance undergoing oxidation is

(a) H_2O_2 *(b)* Na_2CO_3 *(c)* Na_2O_2 *(d)* None of these

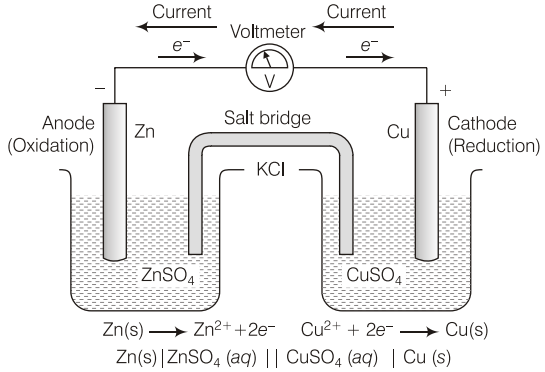
Sol. ***(d)*** $\overset{-1}{H_2O_2} + \overset{+1}{Na_2}\overset{+4\,-2}{CO_3} \longrightarrow \overset{+1}{Na_2}\overset{-1}{O_2} + \overset{+4\,-2}{CO_2} + \overset{-2}{H_2O}$

None of the elements changes its oxidation number.

Electrochemical cell

The device through which chemical energy changes to electrical energy is called **electrochemical cell** or **voltaic cell** or **galvanic cell**. The change of chemical energy to electrical energy causes lowering of free energy, which appears as electrical energy and measured in terms of emf. In an electrochemical cell, the potential produced by an electrochemical reaction depends on the oxidising agents and reducing agents used as reactants.

- As we know, redox reactions can be split into two half-reactions. Hence, in an electrochemical cell these two half reactions occur at two different electrodes, which most often consist of metal plates or wire.
- Electrochemical cell consists of two compartments, each of which is called a half-cell joined by a salt bridge. Each half-cell consists of an electrode dipped in a solution of same or different solution of electrolyte.
- These half-cells are designed to undergo the oxidation half-reaction and reduction half-reaction separately.



Electrode Potential

The electrode potential is a measure of the tendency of an electrolyte to gain or lose electrons in the half-cell, or it is defined as the potential difference set-up between an electrode and its solution.

Classification of Electrode Potential

Oxidation potential	Reduction potential
The tendency of an electrode to lose electrons or to get oxidised is known as oxidation potential (E_{oxi})	The tendency of an electrode to gain electrons or to get reduced is known as reduction potential (E_{red})
e.g. $M(s) \rightleftharpoons M^{n+}(aq) + ne^-$	e.g. $M^{n+}(aq) + ne^- \rightleftharpoons M(s)$
$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$	$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$
Such an electrode is negatively charged with respect to its salt solution.	Such an electrode is positively charged with respect to its salt solution.

$$E_{oxi} = -E_{red}$$

The half-cell reactions are always written as reduction half-reactions and their potentials are represented as reduction potentials.

Standard Electrode Potential ($E°$)

- It is equal to the electrode potential when concentration of electrolytic solution is 1M and temperature is 298 K.
- If the electrode involves in gas phase then, standard conditions chosen are 1 atm pressure of gas, 1 M concentration of its ions and temperature 298K.

Bipotential Electrode Sensors

- Electrocardiography (ECG), electromyography (EMG) and electroencephalography (EEG) systems measure heart, muscle and brain activity respectively over time by measuring electric potentials on the surface of living tissue.
- Nervous stimuli and muscle contractions can be detected by measuring the ionic current flow in the body. This is accomplished using a **biopotential electrode.**
- The current flow in the human body is due to ion flow, not electrons.
- A biopotential electrode is a transducer that senses ion distribution on the surface of tissue and converts the ion current to electron current.

Cell Potential and Electromotive Force (emf)

The difference in potential of two electrodes is known as cell potential. Under standard conditions, the cell potential is known as standard cell potential (E°_{cell}). When no current is drawn from the cell, the maximum possible cell potential is known as emf of the cell. Since, every redox reaction can be thought as the sum of two half-reactions (oxidation and reduction), therefore, we can calculate the cell potential or emf by the addition of two half-cell potential of two half-reactions.

$$E^\circ_{cell} = E^\circ_{oxidation} + E^\circ_{reduction}$$

E°_{cell} = Reduction potential of cathode − Reduction potential of anode

TIPS TO CALCULATE CORRECT CELL POTENTIAL VALUE

In entrance exams, most of the students do common mistakes while solving problems related to calculation of cell potential value. These mistakes can be removed if you follow following conditions :

- You can cross check your final answer whether it is correct or not just by seeing the value of cell potential.
  - For a forward spontaneous reaction, cell potential value should be positive.
  - For a backward spontaneous reaction, cell potential value should be negative.
- Mostly we use reduction potential value for both cells for calculating the cell potential value as follow :

$$E_{cell} = E_{cathode} - E_{anode} = E_R - E_L$$

  - But if oxidation potential of anodic half cell and reduction potential of cathodic half-cell is given then E_{cell} is calculated as,

$$E_{cell} = E_{cathode} + E_{anode} = E_R + E_L$$

- If simply potential value is provided along with cell or half cell reaction, this value is considered same as the corresponding phenomena

e.g. $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu\ ;\ E° = E°_{cell}$

$$Zn \longrightarrow Zn^{2+} + 2e^-;\ E° = E°_{oxidation}$$

$$Zn^{2+} + 2e^- \longrightarrow Zn;\ E° = E°_{reduction} = E°_{Zn^{2+}/Zn}$$

Measurement of Electrode Potential

- The measurement of absolute value of electrode potential is not possible for a single electrode. Only the difference in potential between two electrodes can be measured experimentally. It is due to the reason that oxidation or reduction cannot occur alone rather they occur simultaneously. For indirect measurement of potential of an electrode, we couple one electrode with another electrode whose potential is known. This electrode is called **reference electrode**.
- Now as we know the emf (measured experimentally) as well as the value of reference electrode, the value of other electrode is determined.
- Hydrogen electrode is use as reference electrode. The reason for such a usage is that it can act as a cathode as well as anode with respect to other electrode.

$$H_2(g) \longrightarrow 2H^+ + 2e^-;\ 2H^+ + 2e^- \longrightarrow H_2$$

Example 5 For a cell set-up

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$$

$$Zn^{2+}(aq) \longrightarrow Zn(s) + 2e^-,\ E° = \frac{x}{2}$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s),\ E° = \frac{y}{2}$$

The E°_{cell} for the net cell reaction will be

(a) $\frac{x+y}{2}$ (b) $\frac{x-y}{2}$ (c) $\frac{y-x}{2}$ (d) $\frac{x.y}{2}$

Sol. *(c)* Here, copper half-cell behaves as cathode and zinc half-cell as anode.

$\because \quad E^\circ_{cell} = E^\circ_{(C)} - E^\circ_{(A)}$

$\therefore \quad E^\circ_{cell} = \frac{y}{2} - \frac{x}{2}$

$E^\circ_{cell} = \frac{y-x}{2}$

Example 6 Reduction potentials of some metal ions are given below:

(i) $Al^{2+}/Al, E^\circ = -1.66$ V

(ii) $Co^{2+}/Co, E^\circ = -0.28$ V

(iii) $Cu^{2+}/Cu, E^\circ = +0.34$ V

Which pair will give maximum positive value for E°_{cell}?

(a) (i) and (iii) *(b)* (i) and (ii)

(c) (ii) and (iii) *(d)* All give equal E°_{cell}

Sol. *(a)* $\because E^\circ_{cell} = E^\circ_{(C)} - E^\circ_{(A)}$ and

E° for (i) is most negative and E° for (iii) is positive

Therefore, the maximum E°_{cell} is shown by combination of (i) and (iii).

Electrochemical Series

The arrangement of metals in the decreasing order of tendency to lose electrons is called electrochemical series.

Electrochemical series for some elements is given below

Element	Electrode reaction (reduction)	Standard electrode reduction potential E° (volt)
Li	$Li^+ + e^- \longrightarrow Li$	−3.05
K	$K^+ + e^- \longrightarrow K$	−2.93
Ca	$Ca^{2+} + 2e^- \longrightarrow Ca$	− 2.87
Na	$Na^+ + e^- \longrightarrow Na$	−2.71
H_2	$H^+ + 2e^- \longrightarrow H_2$	0.00
Br_2	$Br_2^+ + 2e^- \longrightarrow 2Br^-$	+1.08
Cl_2	$Cl_2^+ + 2e^- \longrightarrow 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- \longrightarrow Au$	+1.50
F_2	$F_2^+ + 2e^- \longrightarrow 2F^-$	+2.87

Increasing tendency for reduction / Increasing tendency to accept e^- / Increasing strength as oxidising agent

Increasing strength as reducing agent / Increasing tendency to lose electrons / Increasing tendency for oxidation

Characteristics of Electrochemical Series

- Negative sign of standard reduction potential (SRP) indicates that the electrode when joined with standard hydrogen electrode (SHE) behaves as anode. Similarly, positive sign of SRP suggests behaviour of electrode as cathode when joined with SHE.
- The elements which are better reducing agents than hydrogen are placed above hydrogen in this series, while elements which are better oxidising agents than hydrogen are placed below the hydrogen in this series.
- Elements which get oxidised easily are good reducing agents (metals) and elements which get reduced easily are good oxidising agents (non-metals).

Applications of Electrochemical Series

The applications of electrochemical series include.

- In comparing the reactivity of metals.
- In comparing the oxidising and reducing behaviour of elements.
- In the calculation of emf of the cell.
- In predicting the thermal stability of metallic oxide.
- In predicting the feasibility of a reaction.
- In predicting the product of electrolysis.
- In protecting the metal from corrosion.
- In the extraction of metals.

Electrolysis

- It is a process in which electric current is passed through an electrolytic solution in order to bring about a chemical change. In simple words, we can say. "Electrical energy is used to carry chemical reaction in this process."
- Infact, in electrolysis, electric current is used to bring a non-spontaneous chemical reaction.

Electrolytic Cells

- The electrolysis process is carried out in electrolytic cells. These cells contain two electrodes partially dipped in a molten or aqueous solution of an electrolyte. The electrical energy is used to carry out a non-spontaneous reaction.
- The cathode in electrolytic cell is negative as electrons are being forced into it by the external voltage source.
- The anode is positive as electrons are being withdrawn by the external source.

Teacher's NOTE

- In electrochemical cells, chemical energy is converted into electrical energy while in electrolytic cell, electrical energy is converted into chemical energy.
- The reduction and oxidation reactions which occur at respective electrodes during electrolysis are called **primary reactions**.
- Primary reactions are responsible for the discharge of 1 cation type and one anion type out of many present within the solution. e.g. when brine solution (*aq.* NaCl) is electrolysed, H_2 is released (discharged) at cathode and Cl_2 is discharged at anode.

Discharge Potential

It is the potential at which discharge of a cation occurs at cathode or that of an anion occurs at anode.

- The species with lower discharge potential will get discharged first at the electrode.

- If electrolysis is done for an electrolyte consisting more than two ions, it is observed that all the ions are not discharged at the electrodes simultaneously. But certain ions are liberated at electrodes in preference to others.
- The above phenomenon is explained by preferential discharge theory. It states that if more than one type of ions are attracted towards a particular electrode, the ion which discharged first is the one which requires least energy.
- Let us consider the electrolysis of sodium sulphate solution using inert electrodes.
  The reactions involves in electrolysis of *aq*. Na_2SO_4 are,

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + \bar{O}H$$

At cathode $H^+ - e^- \longrightarrow \frac{1}{2}H_2$

At anode $2\bar{O}H \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

- Hydrogen is discharged at cathode as H^+ ions have lower discharge potential than Na^+.
- $\bar{O}H$ ions are discharged at anode as these have lower discharge potential than SO_4^{2-}.
- The net reaction describes the electrolysis of water.
- The ions of Na_2SO_4 conduct the current through the solution and does not take part in the overall reaction.

Correlation of Discharge Potential with Standard Electrode Potential

For Cations

- The species with higher reduction potential will have lower discharge potential. Thus, gets discharged first.
- The species with lower reduction potential will have higher discharge potential. Thus, gets discharged in the last.
- The decreasing order of discharge potential for cations is given below.

$$K^+ > Na^+ > Ca^{2+} > Mg^{2+} > Al^{3+} > Zn^{2+} > H^+ > Cu^{2+} > Hg^{2+} > Ag^+$$

For Anions

- The species with higher oxidation potential will have lower discharge potential. Thus, gets discharged first.
- The species with lower oxidation potential will have higher discharge potential. Thus, gets discharged in the last.
- The decreasing order of discharge potential for anions is given below.

$$SO_4^{2-} > NO_3^- < \bar{O}H > Cl^- > Br^- > I^-$$

Example 7 Reduction potential of four elements *P*, *Q*, *R* and *S* are – 2.90, + 0.34, + 1.20 and – 0.76, respectively. Reactivity decreases in order

(a) $P > Q > R > S$ (b) $S > R > Q > P$
(c) $P > S > Q > R$ (d) $Q > S > R > P$

Sol. **(c)** The reducing power, i.e. the tendency to lose electrons increases as the reduction potential decreases.

Faraday's Law of Electrolysis

Faraday was the first scientist who described the quantitative aspect of electrolysis. He gave two laws of electrolysis, they are as follows

Faraday's First Law It states that, 'mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed'

i.e. $W = Zit$

where, W = substance deposited (in gram)

$i \times t$ = electricity passed per unit time

Z = proportionality constant also called electrochemical equivalent

Thus, electrochemical equivalent is defined as the mass of substance deposited when one coulomb of electricity is passed through a solution.

$$Z = \frac{\text{Equivalent weight of substance}}{96500}$$

96500 = Faraday's constant (F)

Faraday's Second Law It states that 'when same quantity of electricity is passed through solutions of different electrolytes connected in series, the weight of substance produced at the electrodes is directly proportional to their equivalent weights'

i.e. $\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Equivalent weight of Cu}}{\text{Equivalent weight of Ag}}$

Note The above law in modern combined version may be stated as 'the amount of electricity (or charge) required for oxidation or reduction depends upon stoichiometry of the electrode reaction.'

Example 8 Amount of Faraday's required to convert 2 mol of $C_6H_5NO_2$ to $C_6H_5NH_2$ is

(a) 2F (b) 3F (c) 6F (d) 12F

Sol. **(d)** (i) Oxidation number for NO_2^- (for N-atom)

$$x - 4 = -1$$

or $x = +3$

(ii) Oxidation number for NH_2^- (for N-atom)

$$x + 2 = -1$$

or $x = -3$

Thus, change in oxidation number = 6 units per mol

$\therefore$ For 2 moles we need $2 \times 6 = 12$ F of charge.

Applications of Electrolysis

Electroplating

If a metal or other electrical conductor serves as the cathode in an electrolytic cell, the metal can be plated with another metal to protect it against corrosion.

Therefore, the process of depositing a thin film of a metal on another metal by electrolysis is known as electroplating. Generally, electroplating of less reactive metal on more reactive metal prevents the corrosion of more reactive metal and protect it, e.g. electroplating of zinc on iron sheets (here, zinc is less reactive than iron).

For Extraction of Metals

Electrolysis can be used for extracting useful metals. Metals having high values of standard oxidation potential are extracted by electrolysis of their fused salts. While metals having low standard oxidation potentials can be extracted by electrolysis of their aqueous solutions.

For the Production of Some Important Gases and Compounds

Gases like H_2, O_2, F_2, Cl_2 etc., and compounds like NaOH, $KClO_3$, $K_2S_2O_8$, H_2O_2 etc., are obtained by electrolysis.

Smart Practice

1. The correct statement about an electrochemical cell is
(a) In a galvanic cell, cathode is rich in electrons and force them towards anode
(b) In a Daniell cell, loss in mass at anode electrode is equal to the gain in mass at cathode electrode
(c) When external potential becomes equal to cell potential, an electrochemical cell provides maximum current
(d) When external potential increases more than cell potential, the cell starts to act as an electrolytic cell

2. On passing the current of 9.65 A per hour, volume of 0.1 M $FeSO_4$ (aq) oxidised in 1 h will be
(a) 9.6 L *(b)* 0.1 L *(c)* 3.6 L *(d)* 1.8 L
Hint Number of equivalents of electricity $(n') = \frac{i \times t}{96500}$
Number of equivalents $(n') = N \times V$ (in L)
$N = C \times Z$ (C = molarity, Z = equivalent factor) $n' = C \times Z$

3. A gas G is bubbled through a solution of $M^{\oplus}P^{\ominus} + M^{\oplus}Q^{\ominus}$ at 25°C, the order of standard reduction potential is $Q > P > G$.
The correct statement is
(a) P will oxidise G, but not Q *(b)* Q will oxidise P, but not Q
(c) G will oxidise both Q and P *(d)* P will reduce G, but not Q
Hint More positive be the reduction potential, more easily it will get reduced to behave as more stronger oxidising agent.

4. An alcohol detecting meter (breathalyzer) is used to detect alcohol content in drunken drivers. The ethanol present in the alcohol, oxidises to ethanoic acid with acidic solution of $K_2Cr_2O_7$ as follows

$$3C_2H_5OH\,(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \longrightarrow 3CH_3COOH + 4Cr^{3+}(aq) + 11\,H_2O.$$

If, $E^\circ_{(CH_3COOH/C_2H_5OH)} = 0.06$ V
and $E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V

$E^\circ_{(cell)}$ of the reaction taking place in the alcohol meter will be
(a) 1.27 V *(b)* 1.39 V *(c)* 1.31 V *(d)* 1.34 V
Hint $\because E^\circ_{Cell} = E^\circ_{oxi} + E^\circ_{red}$

5. For a redox reaction, $2Cu^+ \longrightarrow Cu^{2+} + Cu$,
if $E^\circ_{(Cu^+/Cu)} = 0.60$ V; $E^\circ_{(Cu^{2+}/Cu)} = 0.326$ V
$E^\circ_{(Cu^{2+}/Cu^+)} = 0.16$ V
The value of E°_{cell} will be
(a) + 0.44 V *(b)* − 0.44 V *(c)* + 0.76 V *(d)* − 0.76 V

6. A voltaic cell is made by using an unknown electrode (Z) and a silver electrode. The cell notation is as follows

$$Z(s)\,|\,Z^{2+}(1.0\ M)\,||\,Ag^+(0.1\ M)\,|\,Ag(s)$$

$E^\circ_{(Ag^+/Ag)} = 0.8$ V and $E^\circ_{cell} = 1.20$ V at 25°C
The standard electrode potential ($E°$) of unknown cell (electrode) and nature of electrode will be, respectively
(a) (−) 0.40 V and acts as strong reducing agent
(b) (+) 0.40 V and acts as strong reducing agent
(c) (−) 2.0 V and acts as strong oxidising agent
(d) (+) 2.0 V and acts as strong oxidising agent
Hint As per given cell notation
$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{Anode}$; $E_{Anode} = 0.8 - 1.20 = -0.4$ V

7. For an electrode Cu/CuS, solubility product (K_{sp}) of CuS $= 4 \times 10^{-32}$ mol/L and $E^\circ_{(oxi)} = -0.442$ V at equilibrium. The $E^\circ_{(red)}$ of the given electrode will be (use log 2 = 0.30 and 0.059 = 0.06)
(a) + 0.50 V *(b)* − 8.978 V
(c) + 1.38 V *(d)* − 1.38 V
Hint $E^\circ_{cell} = E^\circ_{red} + E^\circ_{(oxi)}$
$\therefore E^\circ_{cell} = \frac{0.06}{2}\log K_{sp}$

8. 96.5 A current is passed for 1000 s through 10 L of 1 M $CuSO_4$ (aq) solution. The pH of the solution becomes (at. mass of Cu = 63.5, S = 32, O = 16)
(a) pH = 1 *(b)* pH = 0.1 *(c)* pH = 10 *(d)* pH = 0.01
Hint Number of Faradays = $\frac{i \times t}{96500}$
Also, pH = −log $[H^+]$

9. On passing the current of 1 A for 16.08 min through a solution of $CuSO_4$ (*aq*) at NTP, species available at anode and its volume at NTP will be

(a) At anode-$O_2(g)$, Volume at NTP-0.056 L
(b) At anode-$SO_2(g)$, Volume at NTP-0.056 L
(c) At anode-$O_2(g)$, Volume at NTP-0.224 L
(d) At anode-$SO_2(g)$, Volume at NTP-0.224 L

Hint Discharge potential of H_2O is less than that of SO_4^{2-}, thus $O_2(g)$ is present at anode.

Number of equivalent of charge = $\frac{i \times t}{96500}$

10. 1 F and 0.01 F of electricity is passed through 10 L of 1 M NaCl (*aq*) and 1 L of 0.1 M $CuSO_4$ (*aq*) solutions, respectively. pH of NaCl (*aq*) and $CuSO_4$ (*aq*) solution after passing the current will be respectively

(a) 13 and 2 *(b)* 2 and 13 *(c)* 12 and 3 *(d)* 3 and 12

Hint On passing 1 F of electricity through 10 L of 1 M NaCl(*aq*) solution, we get $H_2(g)$ at cathode and $O_2(g)$ at anode.
While on passing 0.01F electricity through 1 L of 0.1 M $CuSO_4$ solution, we get Cu(*s*) at cathode and $O_2(g)$ at anode.

11. The standard potential at 25°C for the following half-reactions are given as

$$Zn^{2+} + 2e^- \longrightarrow Zn \quad E° = -0.762V$$
$$Mg^{2+} + 2e^- \longrightarrow Mg \quad E° = -2.37\ V$$

When zinc is added to the solution of $MgCl_2$

(a) $ZnCl_2$ is formed *(b)* Mg is precipitated
(c) Zn dissolved in the solution *(d)* No reaction takes place

Hint If E^0_{cell} comes out to be negative, then no reaction takes place.

12. When a sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are

Cathode	Anode
(a) pure zinc	pure copper
(b) impure sample	pure copper
(c) impure zinc	impure sample
(d) pure copper	impure sample

13. 9.65 A of current is passed through 100 mL of 1 M $CuBr_2$ (*aq*) solution for 100 s. After passing the current, the normality of the solution becomes

(a) 0.19 N *(b)* 1.90 N *(c)* 0.38 N *(d)* 3.8 N

Hint Normality $N = C \times Z$

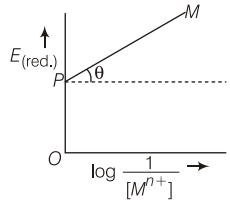
where, C = Molarity, Z = Equivalent factor

Number of equivalents of charge = $\frac{i \times t}{96500}$

14. The relation used to find E_{red} of an electrode is

$$E_{red} = E^\circ_{red} - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]}$$

The plot for the above relation is as follows



On the basis of above information, the correct statement(s) is/are

(i) segment OP represents the value of $E^\circ_{(red)}$.
(ii) on increasing the temperature at constant conc., $E_{(red)}$ increases.
(iii) on increasing the concentration $[M^{n+}]$, $E_{(red)}$ decreases.
(iv) slope of the curve (MP) gives the value $-2.303\frac{RT}{nF}$.

(a) Only (i) *(b)* (i) and (iii)
(c) (i), (ii) and (iii) *(d)* (i), (ii) and (iv)

Hint $E_{(reduction)} \propto [M^{n+}]$. On increasing the concentration $[M^{n+}]$, the value of $E_{(reduction)}$ increases.

15. For the following half-cell reactions, $E°$ values are

$$Mn^{2+}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + 4H^+(aq) + 2e^-, \quad E° = -1.23\ V$$
$$MnO_4^-(aq) + 4H^+(aq) + 3e^- \longrightarrow MnO_2(s) + 2H_2O(l), \quad E° = +1.70\ V$$

(a) Mn^{2+} reacts with MnO_4^- in acidic solution to form MnO_2
(b) $Mn(MnO_4)_2$ is stable in acidic solution
(c) MnO_2 disproportionates to Mn^{2+} and MnO_4^- in acidic solution
(d) None of the above

Hint $3Mn^{2+}(aq) + 2MnO_4^-(aq) + 2H_2O(l) \longrightarrow 5MnO_2(s) + 4H^+$, $E^\circ_{cell} = 0.47\ V$
$E^\circ_{cell} > 0$, hence spontaneous

16. The $E^\circ_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are –0.41 V, +1.57 V, +0.77 V and 1.97 V, respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest?

(a) Cr *(b)* Mn *(c)* Fe *(d)* Co

Hint Cr^{3+}/Cr^{2+} with most negative $E°_{red}$ is the best reducing agent.

17. When Al_2O_3 is electrolysed, cations and anions are discharged. For a given quantity of electricity, ratio of number of moles of Al to O_2 gas is

(a) 1 : 1 *(b)* 2 : 1 *(c)* 2 : 3 *(d)* 4 : 3

Hint When same quantity of electricity is passed, elements/gases are formed in the ratio of their equivalents.

18. Refining of impure metals is done by electrolysis using impure metal as anode. Choose the correct option about refining.

(a) E°_{cell} of the net reaction is zero
(b) metal to be refined, is dissolved in the solution and deposited at the cathode
(c) Both *(a)* and *(b)*
(d) None of the above

Hint At anode (impure) : $M \longrightarrow M^{n+} + ne^-$; $E°_{ox} = xV$
At cathode (pure) : $M^{n+} + ne^- \longrightarrow M$; $E°_{red} = -xV$
M (anode) $\longrightarrow M$ (cathode) ; $E°_{cell} = 0$

19. In the refining of silver by electrolytic method, current of 5A is passed for 2hr using 100g of impure anode of silver of 95% purity. Weight of silver anode after electrolysis is

(a) 40.29 g (b) 59.17 g (c) 57.59 g (d) 42.41 g

Hint Faraday's first law of electrolysis,

$$w = Zit$$

20. Which of the following acts as both an oxidising as well as reducing agent?

(a) HNO_3 (b) HNO_2 (c) HI (d) H_2SO_4

21. If salt bridge is removed from the two half-cells, the voltage

(a) drops to zero (b) does not change

(c) increases gradually (d) increases rapidly

22. An electrochemical cell is set-up as follows

$Pt(H_2, 1\ atm) \mid 0.1\ M\ HCl \mid\mid 0.1\ M CH_3COOH \mid (H_2, 1\ atm)\ Pt$ emf of this cell will not be zero because

(a) the pH of 0.1 M HCl and 0.1 M acetic acid is not same

(b) acids used in two compartments are different

(c) emf of a cell depends on the molarities of acids used

(d) the temperature is constant

Hint The pH of HCl is more because HCl is a strong acid and CH_3COOH is a weak acid.

23. 5A of current is passed through a solution of zinc sulphate for 40 min. Find the amount of zinc deposited at the cathode.

(a) 4.065 g (b) 8.065 g (c) 16.065 g (d) 32.065 g

Hint $W_{metal} = \dfrac{Eit}{96500}$

24. Saturated solution of KNO_3 is used to make salt bridge because

(a) velocities of both K^+ and NO_3^- are nearly the same

(b) velocity of K^+ is greater than that of NO_3^-

(c) velocity of NO_3^- is greater than that of K^+

(d) KNO_3 is highly soluble in water

25. Which of the following facts is/are correct for standard hydrogen electrode?

(a) It is assigned a zero potential at all temperatures corresponding to the reaction, $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$

(b) Platinum electrode coated with platinum black is dipped in acidic solution and H_2 gas is bubbled through it

(c) Concentration of both, oxidised and reduced forms of hydrogen is maintained at unity

(d) All the above facts are correct

26. K_2MnO_4 is converted to MnO_2 by passing 1F of electricity. 1 mole of K_2MnO_4 will form mole of MnO_2 is

(a) 1 (b) 0.5

(c) 0.66 (d) 0.33

27. The standard reduction potential, $E°$ for the half-reactions are as

$Zn \rightleftharpoons Zn^2 + 2e^-$, $E° = +0.76\ V$

$Fe \rightleftharpoons Fe^{2+} + 2e^-$, $E° = +0.41\ V$

The $E°_{cell}$ formed by the above two electrodes is

(a) – 0.35 V (b) – 1.17 V (c) + 0.35 V (d) + 1.17 V

Hint EMF $= E_{cathode} - E_{anode}$

$$Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$$

Oxidation

Reduction

28. What products are formed during the electrolysis of a concentrated aqueous solution of sodium chloride using an electrolytic cell in which electrodes are separated by a porous pot?

I. $Cl_2(g)$ II. NaOH (aq)

III. $H_2(g)$ IV. NaClO (aq)

V. $NaClO_3(aq)$

Select the correct choice.

(a) I and II (b) I, II and V

(c) I, III and V (d) I, II and III

Hint At anode : $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

At cathode : $2Na^+(aq) + 2e^- \longrightarrow 2Na(l)$

$2Na(l) + 2H_2O \longrightarrow 2NaOH(aq) + H_2(g)$

Since, electrodes are separated, therefore no reaction takes place between the products formed at the cathode and anode.

29. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal. The cathode reaction is

$$Al^{3+} + 3e^- \longrightarrow Al$$

To prepare 5.12 kg of aluminium metal by this method would require how many coloumbs of electricity?

(a) 5.49×10^1 C (b) 5.49×10^4 C (c) 1.83×10^7 C (d) 5.49×10^7 C

Hint $W = ZQ$

Where, $Z = \dfrac{\text{Equivalent weight}}{96500}$

30. When the electric current is passed through a cell having an electrolyte, the positive ions move towards cathode and negative ions towards the anode. If the cathode is pulled out of the solution

(a) the positive and negative ions will move towards anode

(b) the positive ions will start moving towards the anode while negative ions will stop moving

(c) the negative ions will continue to move towards anode while positive ions will stop moving

(d) the positive and negative ions will start moving randomly.

Answers

1. (d)	**2.** (d)	**3.** (a)	**4.** (a)	**5.** (a)	**6.** (a)	**7.** (b)	**8.** (a)	**9.** (a)	**10.** (a)
11. (d)	**12.** (d)	**13.** (b)	**14.** (d)	**15.** (a)	**16.** (a)	**17.** (d)	**18.** (c)	**19.** (c)	**20.** (a)
21. (a)	**22.** (a)	**23.** (a)	**24.** (a)	**25.** (d)	**26.** (d)	**27.** (c)	**28.** (d)	**29.** (d)	**30.** (d)

EAMCET (TS) 2016
SOLVED PAPER
Engineering Entrance Examination

Held on : 15 May, 2016

INSTRUCTION

- All questions are compulsory.
- The question paper consists of 40 questions.
- There is no overall choice. However, internal choices has been provided. You have to attempt only one of the alternatives in all such questions.
- Use of calculator is not permitted.

EXAM CRUX

- There were 40 questions asked in EAMCET(TS) engineering entrance exam, out of which 5 to 6 questions were numerical based, while 34 to 35 were theory based. Overall paper was simple. Numericals were also simple formula based with simple calculation.
- According to chapterwise distribution, number of questions were asked as:

For Class XI

- Some Basic Concepts of Chemistry-1Q, Structure of Atom-2Qs, Periodic Properties-2Qs, Chemical Bonding-2Qs, States of Matter-2Qs, Thermodynamics-1Q, Equilibrium-2Qs, Redox Reactions-2Qs, The *s*-Block elements-2Qs, The *p*-Block Elements-1Q and Environmental Chemistry-1Q.

From Class XII

- The Solid State-1Q, Solutions-2Qs, Electrochemistry-1Q, Chemical Kinetics-1Q, Surface Chemistry-1Q, Metallurgy-1Q, The *p*-block Elements-3Qs, The *d*-and *f*-block Elements-1Q, Coordination compounds-1Q, Haloalkanes and Haloarenes-1Q, Aldehydes, Ketones and Carboxylic Acids-3Qs, Amines-1Q, Biomolecules-1Q, and Chemistry in Everyday life-2Qs.
- Overall Physical, Inorganic and Organic Chemistry contained approximately equal weightage of questions.

Difficulty Level Around 55 to 60% questions can be considered as easy, 20 to 25% were relatively moderate and 20 to 25% were tough.

by **Arihant Team**

1. **Assertion** (A) Atoms with completely filled and half-filled subshells are stable.

Reason (R) Completely filled and half-filled subshells have symmetrical distribution of electrons and have maximum exchange energy.

The correct answer is

(a) (A) and (R) are correct, (R) is the correct explanation of (A)
(b) (A) and (R) are correct, (R) is not the correct explanation of (A)
(c) (A) is correct, but (R) is not correct
(d) (A) is not correct, but (R) is correct

2. The element with the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ is

(a) Cu *(b)* Ca *(c)* Cr *(d)* Co

3. Among the following, the isoelectronic pair(s) is/are

(i) O^{2-}, F^-, Na^+, Mg^{2+}

(ii) Na^+, Mg^+, Al^{3+}, F^-

(iii) N^{3-}, O^{2-}, F^-, Ne

(a) (i) and (ii) *(b)* (i), (ii) and (iii)
(c) (ii) and (iii) *(d)* (i) and (iii)

4. What is the atomic number of the element with symbol Uus?

(a) 117 *(b)* 116 *(c)* 115 *(d)* 114

5. Match the following.

List I	List II
(A) PCl_3	(I) Square planar
(B) BF_3	(II) T-shape
(C) ClF_3	(III) Trigonal pyramidal
(D) XeF_4	(IV) See-saw
	(V) Trigonal planar

Codes

	A	B	C	D		A	B	C	D
(a)	IV	II	I	III	*(b)*	III	V	II	IV
(c)	III	V	II	I	*(d)*	II	IV	III	V

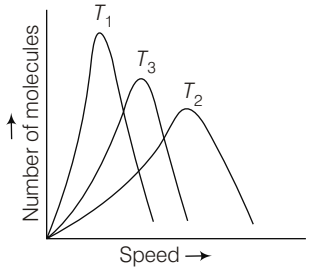
6. The order of covalent character of KF, KI, KCl is

(a) KCl < KF < KI *(b)* KI < KCl < KF
(c) KF < KI < KCl *(d)* KF < KCl < KI

7. If the kinetic energy in J, of CH_4 (molar mass $=16$ g mol^{-1}) at T(K) is X, the kinetic energy in J, of O_2 (molar mass = 32 g mol^{-1}) at the same temperatures is

(a) X *(b)* $2X$ *(c)* X^2 *(d)* $\frac{X}{2}$

8. The given figure shows the Maxwell distribution of molecular speeds of a gas at three different temperatures T_1, T_2 and T_3. The correct order of temperatures is



(a) $T_1 > T_2 > T_3$ *(b)* $T_1 > T_3 > T_2$
(c) $T_3 > T_2 > T_1$ *(d)* $T_2 > T_3 > T_1$

9. In Haber's process, 50.0 g of $N_2(g)$ and 10.0 g of $H_2(g)$ are mixed to produce $NH_3(g)$. What is the number of moles of $NH_3(g)$ formed?

(a) 3.33 *(b)* 2.36 *(c)* 2.01 *(d)* 5.36

10. The following reaction occurs in acidic medium

$KMnO_4 + 8H^+ + 5e^- \rightarrow K^+ + Mn^{2+} + 4H_2O$.

What is the equivalent weight of $KMnO_4$?
(Molecular weight of $KMnO_4 = 158$)

(a) 79.0 *(b)* 31.6 *(c)* 158.0 *(d)* 39.5

11. Given that $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$;

$\Delta_r H° = -92$ kJ, the standard molar enthalpy of formation in kJ mol^{-1} of $NH_3(g)$ is

(a) –92 *(b)* +46 *(c)* +92 *(d)* –46

12. Which one of the following is correct?

(a) The equilibrium constant (K_c) is independent of temperature
(b) The value of K_c is independent of initial concentrations of reactants and products
(c) At equilibrium, the rate of the forward reaction is twice the rate of the backward reaction
(d) The equilibrium constant (K_c) for the reaction $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4$ is, $\frac{[Ni(CO)_4]}{[CO]}$

13. pH of an aqueous solution of NH_4Cl is

(a) 7 *(b)* > 7 *(c)* < 7 *(d)* 1

14. What is the change in the oxidation state of Mn in the reaction of MnO_4^- with H_2O_2 in acidic medium?

(a) 7 → 4 *(b)* 6 → 4 *(c)* 7 → 2 *(d)* 6 → 2

15. Which one of the following will not give flame test?

(a) Ca *(b)* Ba *(c)* Sr *(d)* Be

16. Which one of the following forms a basic oxide?

(a) B *(b)* Tl *(c)* Al *(d)* Ga

17. The gas produced by the passage of air over hot coke is

(a) carbon monoxide *(b)* carbon dioxide
(c) producer gas *(d)* water gas

18. In environmental chemistry, the medium which is affected by a pollutant is called as the .....

(a) sink *(b)* slag *(c)* solvent *(d)* receptor

19. The hybridisation of each carbon in the following compound respectively is

$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - CN$$

(a) sp^3, sp^2, sp^3, sp *(b)* sp^3, sp^3, sp^2, sp
(c) sp^3, sp, sp^3, sp^2 *(d)* sp^3, sp^2, sp, sp^3

20. The product Z of the following reaction is

$$H_3CC \equiv CH \xrightarrow{2HBr} Z$$

(a) $H_3CCH_2CHBr_2$ *(b)* $H_3CCBr_2CH_3$
(c) $H_3CCHBrCH_2Br$ *(d)* $BrCH_2CH_2CH_2Br$

21. Identify X and Y in the following reaction sequence

$$X \xrightarrow{Zn} Y \xrightarrow[Zn\text{-}H_2O]{O_3} (CH_3)_2CO + CH_2O$$

	X	Y
(a)	$(CH_3)_2\underset{\displaystyle Br}{\underset{\|}{C}}HCH_3$	$CH_3CH=CHCH_3$
(b)	$(CH_3)_2CHCH_2Br$	$CH_3CH=CHCH_3$
(c)	$(CH_3)_2CBrCH_2Br$	$(CH_3)_2C=CH_2$
(d)	$(CH_3)_2CHCHBr_2$	$(CH_3)_2C=CH_2$

22. The packing efficiency of simple cubic (sc), body centred cubic (bcc) and cubic close packing (ccp) lattices follow the order

(a) bcc<ccp<sc *(b)* ccp<bcc<sc
(c) sc<ccp<bcc *(d)* sc<bcc<ccp

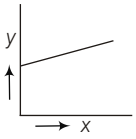
23. The experimental depression in freezing point of a dilute solution is 0.025 K. If the van't Hoff factor (i) is 2.0, the calculated depression in freezing point (in K) is

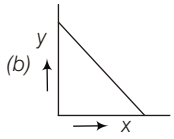
(a) 0.00125 *(b)* 0.025 *(c)* 0.0125 *(d)* 0.05

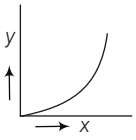
24. The molality of an aqueous dilute solution containing non-volatile solute is 0.1 m. What is the boiling temperature (in °C) of solution? (Boiling point elevation constant, $K_b = 0.52$ kg mol^{-1} K; boiling temperature of water = 100° C).

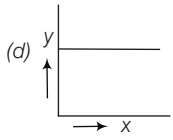
(a) 100.0052 *(b)* 100.052 *(c)* 100.0 *(d)* 100.52

25. Which one of the following is correct plot of Λ_m (in S cm^2 mol^{-1}) and $\sqrt{C}$ (in (mol/L)$^{1/2}$) for KCl solution? ($y = \Lambda_m$; $X = \sqrt{C}$)

(a) 

(b) 

(c) 

(d) 

26. For the reaction

$$5Br^-(aq) + 6H^+(aq) + BrO_3^-(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

if, $-\frac{\Delta[BrO_3^-]}{\Delta t} = 0.01 \text{ mol L}^{-1}\text{min}^{-1}$,

$\frac{\Delta[Br_2]}{\Delta t}$ in mol L^{-1}min^{-1} is

(a) 0.01 *(b)* 0.3 *(c)* 0.03 *(d)* 0.005

27. Which one of the following is an emulsion?

(a) Milk *(b)* Soap lather
(c) Butter *(d)* Vanishing cream

28. Copper matte contains ..... .

(a) Cu_2O, Cu_2S *(b)* Cu_2O,FeO *(c)* Cu_2S,FeS *(d)* Cu_2S,FeO

29. X reacts with dilute nitric acid to form 'laughing gas'. What is X ?

(a) Cu *(b)* P_4 *(c)* S_8 *(d)* Zn

30. Xenon reacts with fluorine at 873 K and 7 bar to form XeF_4. In this reaction, the ratio of xenon and fluorine required is

(a) 1 : 5 *(b)* 10 : 1 *(c)* 1 : 3 *(d)* 5 : 1

31. Which of the following metal ions has a calculated magnetic moment value of $\sqrt{24}$ BM?

(a) Mn^{2+} *(b)* Fe^{2+}
(c) Fe^{3+} *(d)* Co^{2+}

32. Which one of the following does not exhibit geometrical isomerism?

(a) Octahedral complex with formula [MX_2L_4]
(b) Square planar complex with formula [MX_2L_2]
(c) Tetrahedral complex with formula [$MABXL$]
(d) Octahedral complex with formula [$MX_2(L-L)_2$]

33. The polydispersity index (PDI) of a polymer is ($\overline{M}_w$ = weight average molecular mass and $\overline{M}_n$ = number average molecular mass)

(a) the product of $\overline{M}_n$ and $\overline{M}_w$
(b) the sum of $\overline{M}_n$ and $\overline{M}_w$
(c) the difference between $\overline{M}_w$ and $\overline{M}_n$
(d) the ratio between $\overline{M}_w$ and $\overline{M}_n$

34. Hormone that maintains the blood glucose level within the limit is

(a) thyroxine *(b)* insulin
(c) testosterone *(d)* epinephrine

35. Chloroxylenol is an example of ..... .

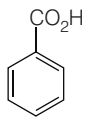
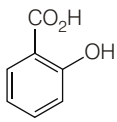
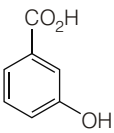
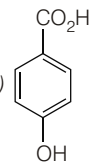
(a) antiseptic *(b)* antipyretic
(c) analgesic *(d)* tranquiliser

36. Which one of the following has highest boiling point?

(a) $H_3CCH_2CH_2CH_2Cl$ *(b)* $(H_3C)_2CHCH_2Cl$
(c) $(H_3C)_3CCl$ *(d)* $H_3CCH_2C(Cl)HCH_3$

37. $X + Y \xrightarrow{H^+}$ Aspirin + H_3CCOOH

Here, X and Y are

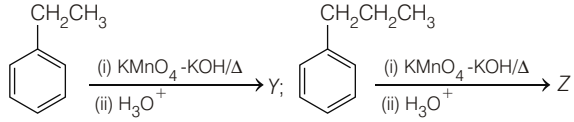
	X	Y
(a)		H_3CCOCl
(b)		$(H_3CCO)_2O$
(c)		H_3CCO_2H
(d)		H_3CCOCH_3

38. $R\text{–}CN \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } SnCl_2 + HCl} R\text{–}CHO$

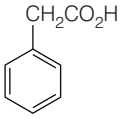
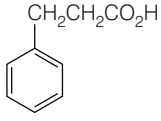
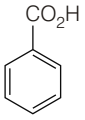
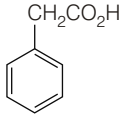
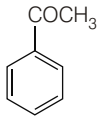
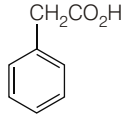
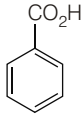
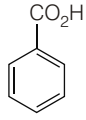
What is the name of the above reaction?

(a) Rosenmund *(b)* Williamson
(c) Stephen *(d)* Kolbe

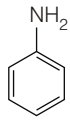
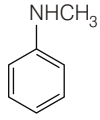
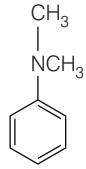
39. Consider the following reactions,



What are the structures of *Y* and *Z*?

	Y	*Z*
(a)		
(b)		
(c)		
(d)		

40. Which is the strongest base among the following?

(a) H_3CNH_2 (b)  (c)  (d) 

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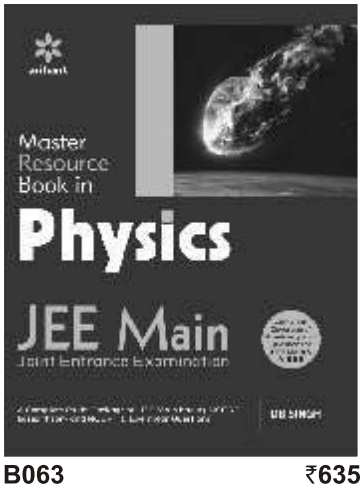
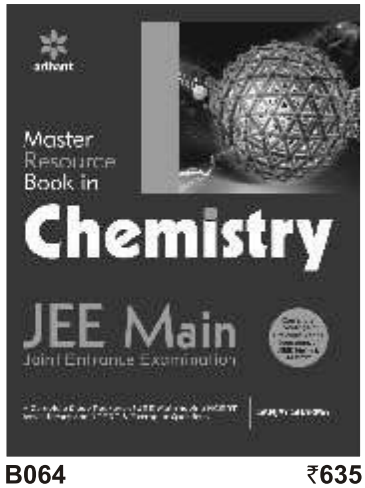
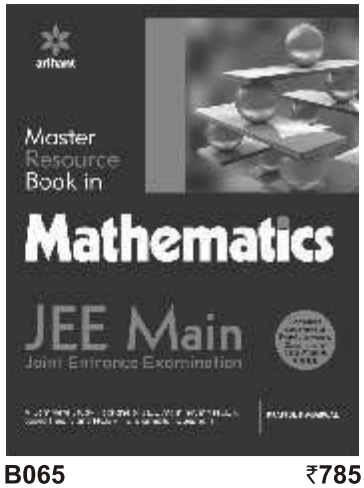


B063 ₹635



B064 ₹635



B065 ₹785

Answers with Explanation

1. ***(a)*** The extra stability of half-filled and fully filled electronic configurations can be explained in terms of symmetry and exchange energy. All the orbitals of the same subshell are either completely filled or half-filled have more symmetrical distribution of electrons. Consequently, their shielding to one another is relatively small and the electrons are more strongly attracted by the nucleus. This leads to more stability of the atom.

2. ***(a)*** The element copper has atomic number = 29

Electronic configuration of Cu

$$=1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1=[Ar]3d^{10}\,4s^1$$

3. ***(d)*** Isoelectronic species are elements or ions that have the same or equal number of electrons.

Hence, $O^{2-}, F^-, Na^+, Mg^{2+}$, Ne, N^{3-}, Al^{3+} are isoelectronic species (all have 10 electrons).

But Mg^+ $11e^-$ is not an isoelectronic with respect to other species.

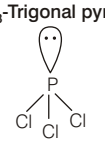
4. ***(a)*** The atomic number of the element Uus is 117.

Ununseptium (Uus) is the second heaviest known element and penultimate element of the 7th period of the periodic table.

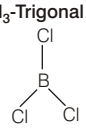
Electronic configuration of Uus = $[Rn]\,5f^{14}\,6d^{10}\,7s^2\,7p^5$.

5. ***(c)*** A → III; B → V; C → II; D → I

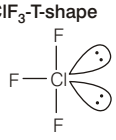
PCl_3-Trigonal pyramidal



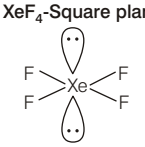
BCl_3-Trigonal planar



ClF_3-T-shape



XeF_4-Square planar



6. ***(d)*** **Thinking process** *Covalent increases with increase in size of anion or decreases with size of cation.*

As, here cation (K^+) in all the species is common, hence the covalent character will increase in the order KF < KCl < KI.

7. ***(a)*** At same temperature, kinetic energy of both the gases will be same, i.e.

$\because$ $KE \propto \sqrt{T}$ (for all gases)

$\therefore$ $KE_{(CH_4)} = KE_{(O_2)} = X$

8. ***(d)*** At lower temperatures , the molecules have less energy. Hence, the molecular speeds are lower, and distribution of molecules has smaller range. But as the temperature increases, distribution range flattens. Hence, correct order is : $T_2 > T_3 > T_1$

9. ***(a)*** **Thinking process**

- *Number of moles of ammonia produced depends upon limiting reagent.*
- *First, find out limiting reagent.*
- *Apply mole concept on limiting reagent and produced* NH_3 *and calculate number of moles of* NH_3 *produced.*

The reaction proceeds as :

$$\underset{28\text{ g}}{N_2(g)} + \underset{6\text{ g}}{3H_2(g)} \rightleftharpoons \underset{34\text{ g}}{2NH_3(g)}$$

$\because$ 6 g H_2 reacts with 28 g N_2

$\therefore$ 10 g H_2 reacts with $\frac{28}{6}\times 10 = 46.67$g N_2,

i.e. H_2 is limiting reagent and N_2 is in excess.

Now,

$\because$ 6 g H_2 produces 34 g NH_3.

$\therefore$ 10 g H_2 will produce $\left(\frac{34}{6}\times 10\right)$ g NH_3.

Therefore, we can calculate number of moles of NH_3 as

$$n_{NH_3} = \frac{\text{Produced weight}}{\text{Molecular weight}} = \frac{\left(\frac{34}{6}\times 10\right)}{17} = \frac{34}{6}\times\frac{10}{17} = \frac{10}{3} = 3.33$$

10. ***(b)*** In the reaction (in acidic medium),

$KMnO_4 + 8H^+ + 5e^- \longrightarrow K^+ + Mn^{2+} + 4H_2O$

$KMnO_4$ acts as an oxidising agent in acidic medium because, it gains 5 electrons from reductant.

$\therefore$ Equivalent weight of $KMnO_4 = \frac{158}{5} = 31.6$ (in g/equivalent)

11. ***(d)*** Given, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta_r H^\circ = -92$ kJ

Chemical reaction for molar enthalpy of formation of NH_3,

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \quad (\Delta_f H^\circ \text{ for } N_2 \text{ and } H_2 = 0)$$

Therefore, $\Delta_f H^\circ = \frac{-\Delta_r H^\circ}{2} = \frac{-92}{2} = -46\text{ kJ mol}^{-1}$

12. ***(b)*** Correct option is (b). (a), (c) and (d) are incorrect.

(a) K_c depends on temperature.

(c) At equilibrium, both the rates are equal.

(d) $K_c = \frac{[Ni(CO)_4]}{[CO]^4}$

13. ***(c)*** **Short trick** *All salts formed by weak base and strong acid show acidic nature in their aqueous solutions.*

Ammonium chloride is a salt of weak base (NH_3) and strong acid (HCl) hence, it is acidic in nature.

$NH_3 + HCl \longrightarrow NH_4Cl$ pH of $NH_4Cl < 7$

14. ***(c)*** Manganese exhibits oxidation states of + 2, + 3, + 4, + 6 and + 7.

Reaction involved when $KMnO_4$ reacts with H_2O_2 in acidic medium,

$2MnO_4^-(aq) + 5H_2O_2(aq) + 16H^+(aq) \rightarrow 2Mn^{2+} + 5O_2(g) + 8H_2O$

So, in acidic medium on reaction of MnO_4^- with H_2O_2 oxidation state of Mn changes from 7 to 2.

15. ***(d)*** **Short trick** *The elements with smaller sizes or the elements in which electrons are bounded towards the nucleus tightly do not give flame test.*

All the elements given in the option belong to group 2. Among which, beryllium is smaller in size, its electrons are more tightly bounded as compare to other. That's why, its outermost electrons do not get excited significantly during flame test.

16. ***(b)*** **Short trick** *More the element has metallic character, more basic is its oxide.*

As the metallic character increases down the group hence, thallium (Tl) has highest metallic character (among the given options) and it forms the basic oxide. Al and Ga form amphoteric oxide and B (Boron) forms acidic oxide.

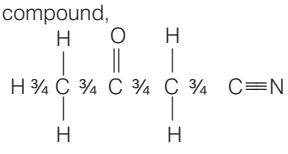
17. ***(c)*** Tha gas produced by passage of air over hot coke is called producer gas. The reaction proceeds as:

$$\underset{\text{Coke}}{2C} + \underbrace{O_2 + N_2}_{\text{(From air)}} \xrightarrow{\Delta} \underbrace{2CO + N_2}_{\text{Producer gas}}$$

Other carbonaceous (carbon containing) fuels also produce producer gas of different compositions.

18. ***(d)*** In environmental chemistry, the medium which is affected by a pollutant is called receptors or targets. Receptors, are the biotic or abiotic components, which affected adversely by the pollution .

19. ***(a)*** In the compound,



(i) sp^3 (ii) sp^2 (iii) sp^3 (iv) sp

The C-atoms that is bonded to four other atoms involve four orbitals (1of *s* and 3 of *p*- orbitals) during hybridisation. Hence, they have sp^3-hybridisation as in cases of (i) and (iii).

The C– atom bonded to three other atoms involves three orbitals (1 of *s* and 2 of *p*-orbitals). Hence, carbon (ii) has sp^2-hybridisation.

The C-atom bonded to two other atoms involves two orbitals (1*s* and 1*p*-orbitals). Hence, carbon (iv) has *sp*- hybridisation.

20. ***(b)*** $H_3CC \equiv CH \xrightarrow{2HBr} H_3CCBr_2CH_3$

The reaction follows Markownikoff's addition.

21. ***(c)*** In this reaction,

$$\underset{(X)}{(CH_3)_2CBr\,CH_2Br} \xrightarrow{Zn} \underset{(Y)}{(CH_3)_2C{=}CH_2} + ZnBr_2$$

$$(Y) \xrightarrow[Zn\text{-}H_2O]{O_3\,(Ozonolysis)} \underset{\text{Acetone}}{(CH_3)_2CO} + \underset{\text{Formaldehyde}}{CH_2O}$$

22. ***(d)*** **Short trick**

- *Packing efficiency of a cubic system* $= \dfrac{\text{Volume occupied by atoms in unit cell}}{\text{Total volume of the unit cell}}$
- *Put values of volume occupied by atoms and total volume of the unit cell in the above formula for sc, bcc and ccp.*
- *Try to maintain same denominator or numerator for all cubic systems.*
- *If denominator is same, then the cubic system with maximum value of numerator will show highest packing efficiency.*
- *If numerator is same, then the cubic system with minimum value denominator will show highest packing efficiency.*

Packing efficiency for simple cubic

$$\frac{\frac{4}{3}\pi r^3}{a^3} \times 100 = \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100$$

$$= \frac{4\pi r^3}{3} \times \frac{1}{8r^3} \times 100 = \frac{100\pi}{6} = 52.4\%$$

For body centred $= \dfrac{2 \times \frac{4}{3}\pi r^3}{\frac{64r^3}{3\sqrt{3}}} \times 100$

$$= \frac{8\pi r^3}{3} \times \frac{3\sqrt{3}}{64r^3} \times 100$$

$$= \frac{\sqrt{3}\pi \times 100}{24}$$

$$= \frac{\sqrt{3}\pi \times 25}{6} = 68\%$$

For cubic closed packing $= \dfrac{4 \times \frac{4}{3}\pi r^3}{32r^3/\sqrt{2}} \times 100$

$$= \frac{16\pi r^2}{3} \times \frac{\sqrt{2}}{32r^2} \times 100 = \frac{\sqrt{2} \times 100}{6} = 74\%$$

Hence, sc < bcc < ccp.

23. ***(c)*** Given, depression in freezing point of a dilute solution is 0.025 K, $i = 2.0$

van't Hoff factor

$$(i) = \frac{\text{Observed colligative property (experimental)}}{\text{Calculated colligative property}}$$

$$2.0 = \frac{0.025}{\text{Calculated colligative property}}$$

Calculated depression in freezing point = 0.0125 K

24. ***(b)*** Given, $K_b = 0.52\ \text{kg mol}^{-1}\ \text{K}$

Boiling point of water = 100°C

$$m = \frac{\Delta T_b}{K_b},\ 0.1 = \frac{\Delta T_b}{0.52},\ \Delta T_b = 0.052$$

Boiling point of solution $(T_b) = 100 + \Delta T_b$

$$= 100 + 0.052 = 100.052$$

25. ***(b)*** Molar conductivity is given as $\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$

Thus, as the $\sqrt{C}$ increases, Λ_m decreases.

26. ***(c)*** $5Br^-(aq) + 6H^+(aq) + BrO_3^-(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

Since, we have $-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = +\frac{1}{3}\frac{\Delta[Br_2]}{\Delta t}$

$$\therefore\ -\frac{\Delta[BrO_3^-]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} \quad \text{Þ} \quad \frac{\Delta[Br_2]}{\Delta t} = -3\frac{\Delta[BrO_3^-]}{\Delta t}$$

$$= 3 \times 0.01 = 0.03$$

27. ***(a)*** Milk is an emulsion of fat and water. An emulsion is a dispersion of tiny droplets of one liquid into another liquid. Thus, it is a liquid-liquid colloidal system.

28. ***(c)*** Copper matte contains Cu_2S and FeS.
On roasting the copper ore, i.e. copper pyrite ($CuFeS_2$), the impurities of S and Fe are converted into cuprous sulphide and ferrous sulphide, respectively.

$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$

29. ***(d)*** Zn reacts with dilute nitric acid to form 'laughing gas'.

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + \underset{\text{Laughing gas}}{N_2O} + 5H_2O$$

30. ***(a)*** XeF_4 is obtained by heating a mixture of xenon and fluorine in the molar ratio of 1 : 5 at 873K and 7 bar pressure in an enclosed nickel vessel for a few hours. The reaction proceeds as

$$Xe(g) + 2F_2(g) \xrightarrow[7\text{ bar}]{\text{Ni-tube, 873K}} XeF_4$$

The extra fluorine taken increases the production.

31. ***(b)*** **Thinking process** *Magnetic moment* (μ) *is related to number of unpaired electron 'n', as*

$$\mu_{eff} = \sqrt{n(n+2)}\ BM$$

$$\mu_{eff} = \sqrt{24}\ BM$$

$$\sqrt{n^2+2n} = \sqrt{24}$$

By removing square root from both sides, we get

$$n^2 + 2n = 24$$

$$\Rightarrow n^2 + 2n - 24 = 0$$

$$\Rightarrow n^2 + 6n - 4n - 24 = 0$$

$$\Rightarrow n(n+6) - 4(n+6) = 0$$

$$\Rightarrow (n-4)(n+6) = 0$$

$$\Rightarrow n = 4 \text{ or } -6$$

– 6 value is not possible, as negative upaired electron will not occur.

Thus, $n = 4$ or we can say the metal ion which have four unpaired electrons will have $\sqrt{24}$ BM magnetic moment.

Out of given options, Fe^{2+} has 4 unpaired electrons as

$Fe^{2+} = [Ar]$ $\boxed{\uparrow\downarrow}\ \boxed{1}\ \boxed{1}\ \boxed{1}\ \boxed{1}$ $(3d^6)$ $\quad \boxed{\ }$ $(4s^0)$

32. ***(c)*** All the other three exhibit geometrical isomerism but tetrahedral complex does not.

33. ***(d)*** The polydispersity index (PDI) of a polymer is the ratio of $\overline{M}_w$ and $\overline{M}_n$. PDI $= \dfrac{\overline{M}_w}{\overline{M}_n}$

For natural polymer, PDI = 1

$\therefore \overline{M}_w = \overline{M}_n$ and polymer is monodispersed

For synthetic polymer, PDI > 1

$\therefore \overline{M}_w > \overline{M}_n$ and polymer is polydispersed.

It is directly related to the standard deviation of polymer molecular weight distribution. Polydispersity index can be used as a measure of the width of the molecular weight distribution.

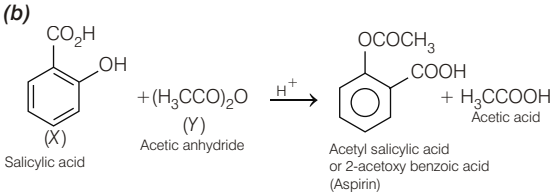
34. ***(b)*** Insulin is a peptide hormone secreted from pancreas. It regulates the blood glucose level metabolism within the limit by signaling liver, muscles and fat cells to take up extra glucose from blood.

35. ***(a)*** Chloroxylenol is an example of antiseptic. Dettol is a mixture of chloroxylenol and α-terpineol. Chloroxylenol is responsible for the antiseptic and disinfectant properties of dettol.

36. ***(a)*** $H_3CCH_2CH_2CH_2Cl$

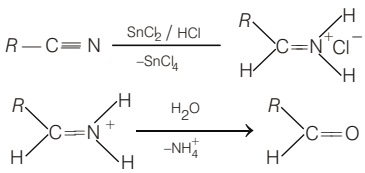
For isomeric alkyl halides, the boiling point decreases with branching. Branching of the chain makes the molecule more compact and therefore, the surface area decreases. Hence, the intermolecular attractive forces which depend upon the surface area, also become small in magnitude due to branching. Consequently, the boiling points of the branched chain having same molecular formula are less than the straight chain isomers. Higher the molecular weight, higher is the boiling point, but branching reduces boiling point.

37. ***(b)***

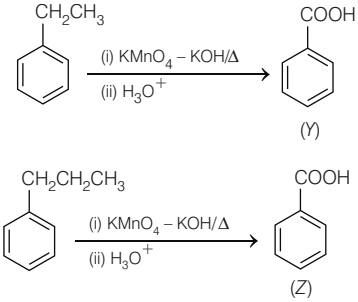


38. ***(c)*** Specifically, when reduction is carried out with $SnCl_2$/HCl. It is called Stephen's reaction.

The generalised reaction looks like

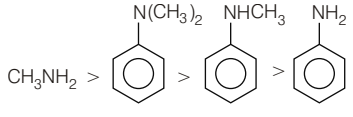


39. ***(d)*** **Short trick** $KMnO_4$ *(alk.) oxidises alkyl group (R) directly attached to benzene ring, irrespective of length of alkyl group (if has at least one* α–H).



40. ***(a)*** **Thinking process** *The species having more lone pair of electrons for donation act as strong base.*

In case of CH_3NH_2, lone pair of electrons on N-atom is available for donation. In other cases N-atom is directly attached to benzene ring thus, lone pair of electron on N-atom is not available for donation (due to delocalisation). Hence, CH_3NH_2 is most basic. Order of basic nature of the given compounds is



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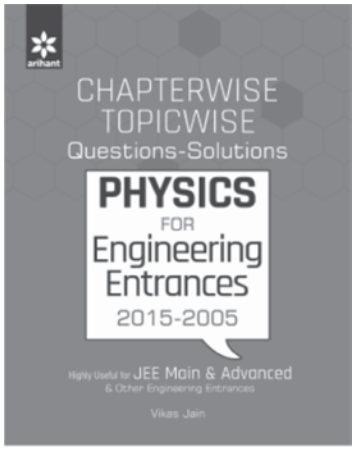

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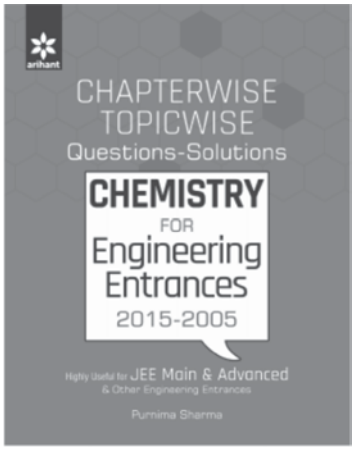

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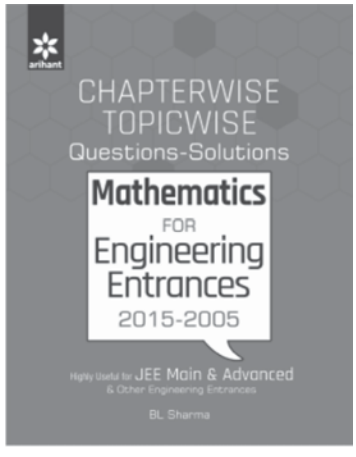

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arihant

NUCLEOPHILIC SUBSTITUTION

A BIRD'S EYEVIEW

Coverage of Special Topics for JEE Advanced

Nucleophilic substitution reactions are the reactions in which a weak nucleophile (leaving group) is replaced from a substrate by a strong nucleophile. There are three components required for nucleophilic substitutions reaction : *substrate*, *nucleophile* and *solvent*. In case of haloalkanes or haloarenes, carbon-halogen bonds are generally polar and nucleophile attacks at the slightly positive carbon atom in $\overset{\delta+}{C}—\overset{\delta-}{X}$ bond, which lead to the nucleophile replacing halide ion X^-.

The outline of these reactions is given as,

$$\underset{\text{Substrate}}{R—X} + \underset{\text{Nucleophile}}{:Z} \xrightarrow{\text{Solvent}} R—Z + \underset{\text{Leaving group}}{:X}$$

Where, R is alkyl or aryl group

Nucleophilicity

- Nucleophilicity refers to the capacity of a Lewis base to participate in a nucleophilic substitution reaction and is contrasted with basicity.
- It is used to describe trends in the rates of substitution reactions that are attributed to properties of the nucleophile.
- There is often competition between displacement (nucleophilicity) and elimination (proton removal, basicity).
- The rate of a substitution reaction is directly related to the effectiveness of the nucleophile in displacing the leaving group.
- There are several properties that can influence nucleophilicity.

(i) **The solvation of the nucleophile**

Strong solvation lowers the energy of an anionic nucleophile. Thus, decreases nucleophilicity.

(ii) **The strength of carbon-halogen bond**

The polarisation of the carbon-halogen bond explains why haloalkanes or haloarenes react with nucleophiles in the nucleophilic substitution reactions. A nucleophile attacks the electron deficient carbon atom of the haloalkane and this leads to the substitution of the halogen atom (X) by the nucleophile. With the exception of iodine, all of the other halogens are more electronegative than carbon, so C—F, C—Cl and C—Br bonds are polar. The electrons in the bond are attracted towards the halogen atom, leading to a partial negative charge ($-\delta$) on F, Cl or Br and a partial positive charge ($+\delta$) on carbon.

(iii) **The electronegativity of the attacking atom**

A more electronegative atom binds its electrons more tightly than a less electronegative one. Thus, high electronegativity of attacking atom is unfavourable in substitution reaction. Thus, $\text{Nucleophilicity} \propto \frac{1}{\text{Electronegativity}}$

(iv) **The polarisability of the attacking atom**

Polarisability describes the ease of distortion of the electron density on the nucleophile. Thus, more distorted the attacking atom, the better its nucleophilicity.

(v) **The structure of the nucleophile**

A more sterically hindered nucleophile is less reactive than a less hindered one.

Note Even though the C—I bond is not polar, iodoalkanes undergo nucleophilic substitution reactions. This is because, when a nucleophile approaches the C—I bond, the bond becomes polarised and the electrons in the C—I bond move from carbon to iodine so the carbon acquires partially positive charge. Thus, the C—I bond is said to have a high polarisability.

Example 1 Which of the following has the highest nucleophilicity? [IIT 2006]

(a) F^- (b) $\bar{O}H$

(c) $\bar{C}H_3$ (d) $\bar{N}H_2$

Sol. **(c)** Nucleophilicity

$$\propto \frac{1}{\text{Electronegativity of atom bearing negative charge}}$$

$\therefore$ Electronegativity order of given species varies as,

$$F^- > \bar{O}H > \bar{N}H_2 > \bar{C}H_3$$

Hence, nucleophilicity order varies as,

$$\bar{C}H_3 > \bar{N}H_2 > \bar{O}H > F^-$$

Thus, $\bar{C}H_3$ is the strongest nucleophile among the given species.

Types of Nucleophilic Substitution Reactions (S_N)

Nucleophilic substitution reactions are of two types which are given below:

S_N2 reactions or bimolecular reactions	S_N1 reactions or unimolecular reactions
Here, 2 stands for molecularity of reactions means these are bimolecular reactions.	Here, 1 stands for molecularity of reactions means these are unimolecular reactions.
Characteristics	
Rate of reaction depends upon the concentration of two species, i.e. substrate and nucleophile.	Rate of reactions depends upon the concentrations of one species, i.e. substrate.
The addition of nucleophile and departure of leaving group takes place simultaneously.	First a planar carbocation is formed which further, reacts with a nucleophile.
S_N2 reaction occurs where the central carbon atom is easily accessible to the nucleophile.	S_N1 reaction occur where central carbon atom is sterically hindered.
Conditions which affect the rate of reaction	
(i) Effect of solvent	
For S_N2 reactions, an aprotic solvent such as acetone, DMF, or DMSO is used because aprotic solvents do not furnish H^+ ions into the solution (If protons are present in S_N2 reactions these will react with a nucleophile and decrease the rate of reactions).	For S_N1 reaction, it is important to use a protic solvent. e.g. water, alcohol etc,. Since, an aprotic solvent attacks the intermediate and cause unwanted product. (The reaction of hydrogen with nucleophile does not cause any effect on the rate of 'reaction' because concentration of nucleophile is not involved in the rate determining step of S_N1 reaction).
(ii) Steric factor	
Since, S_N2 reaction occurs in one step therefore, steric factor decides the rate of reactions.	Since, S_N1 reaction occurs in two steps therefore, steric factor does not decide the rate of reactions. However, stability of intermediate, i.e. carbocation decides the rate of reactions.
(iii) Effect of nucleophilicity	
Greater the nucleophilicity, faster is the rate of reactions.	The rate of these reactions remains unaffected by concentrations of nucleophile.
(iv) Nature of leaving group	
Weakest base is the best leaving group, e.g. $\bar{I} > \bar{B}r > \bar{C}l > F^-$.	Weakest base acts as a best leaving group.
Order of reactivity	
MeX $> 1° > 2° > 3°$.	Benzyl > substituted allyl $> 3° > 2° > 1°$ > MeX.
Catalyst	
Phase transfer catalysts are used e.g. $R_4\overset{+}{N}\bar{X}$, crown ethers etc.	Acids are used as catalysts. e.g. HCl, H_2SO_4, etc.

Example 2 In S_N2 reactions, the correct order of reactivity for the following compounds CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is [IIT 2014]

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

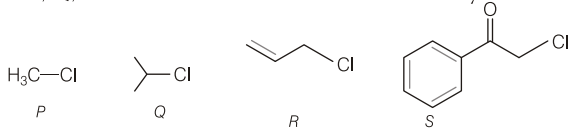
Sol. **(b)** **Strategy** *The order of reactivity towards S_N2 reaction for alkyl halides is*

Primary halides (1°) > Secondary halides(2°) > Tertiary halides(3°)

$$\text{Rate of } S_N2 \text{ reactions} \propto \frac{1}{\text{Steric hindrance on carbon}}$$

CH_3Cl (Less hindered) $>$ CH_3CH_2Cl (1°) $>$ $CH_3-\underset{\underset{CH_3}{|}}{CH}-Cl$ (2°) $>$ $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl$ (3°, More hindered)

Example 3 KI in acetone, undergoes S_N2 reactions with each P, Q, R and S. The rates of the reactions vary as



P Q R S

[JEE Advanced, 2013]

(a) $P > Q > R > S$ (b) $S > P > R > Q$

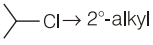
(c) $P > R > Q > S$ (d) $R > P > S > Q$

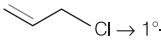
Sol. ***(b)*** **Strategy** *Acetone is an aprotic solvent and can dissolve both the nucleophile and the substrate and thus, S_N2 reaction is favoured.*

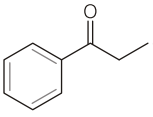
Order of S_N1 reaction *3°-alkyl halide >2 °-alkyl halide > 1°-alkyl halide.*

Order of S_N2 reaction *1°-alkyl halide > 2°-alkyl halide > 3°-alkyl halide*

P. CH_3—Cl → 1°-alkyl halide

Q.  → 2°-alkyl halide, rate is minimum

R.  → 1°-allylic halide but allylic 1° carbocation is resonance stabilised in S_N1 reactions.

S.  → 1°-alkyl halide but C—Cl bond is weak, rate is maximum.

Bond energy is decreased by electron withdrawing group [C_6H_5CO] (a case of-/-effect). Thus, it has maximum rate in S_N2 reaction while 2°-alkyl halide (*Q*) has minimum rate in S_N2 reaction.

Example 4 The order of reactivities of the following alkyl halides for a S_N2 reaction is **[IIT 2007]**

(a) *RF* > *RCl* > *RBr* > *RI*

(b) *RF* > *RBr* > *RCl* > *RI*

(c) *RCl* > *RBr* > *RF* > *RI*

(d) *RI* > *RBr* > *RCl* > *RF*

Sol. ***(d)*** If alkyl groups in alkyl halides are same, the order of leaving ability of halides in S_N2 reactions is given as,

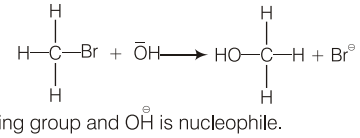
$$F^- < Cl^- < Br^- < I^-$$

Greater the leaving tendency of halide ion, higher will be reactivity of corresponding alkyl halide in S_N2 reaction. Therefore, the order of reactivity of the given alkyl halides is,

RI > *RBr* > *RCl* > *RF*

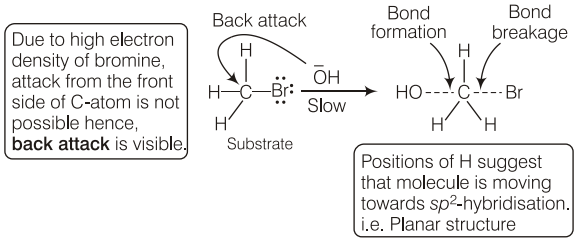
Mechanism of S_N2 reaction

Let us consider the following reaction,

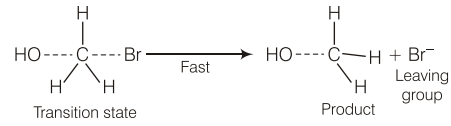


Here, $\overline{Br}$ is leaving group and $\overline{O}H$ is nucleophile.

Step I **Attack of Nucleophile** Attack of $\overline{O}H$ on the primary (1°) alkyl halide (CH_3Br) to form a transition state is shown below.


Due to high electron density of bromine, attack from the front side of C-atom is not possible hence, back attack is visible.
Back attack
Slow
Substrate
Bond formation
Bond breakage
Positions of H suggest that molecule is moving towards sp²-hybridisation. i.e. Planar structure

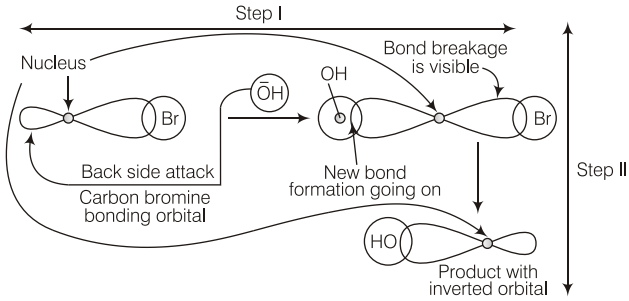
Step II **Formation of Product**



This inversion in configuration of product molecule from the substrate molecule is called **Walden's inversion.**

Look at the position of H and compare it with the one visible in substrate. The opposite configuration suggests that in product molecule the configuration is inverted.

Orbital Picture for S_N2 Reaction



- The product formed here has opposite configuration that of parent reactant. This change in configuration is called **Walden inversion**.
- Step I of this reaction is slower, i.e. formation of transition state is the rate determining step of this reactions. In this step involvement of both substrate and nucleophile suggests that Rate ∝ [Substrate] [Nu^-]

  Hence, the reaction in considered as bimolecular.

Example 5 An S_N2 reaction at an asymmetric carbon of a compound always gives **[IIT 2007]**

(a) an enantiomer of the substrate

(b) a product with opposite optical rotation

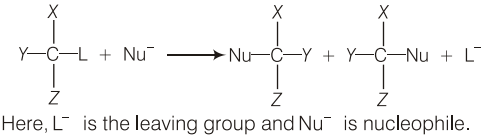
(c) a mixture of diastereomers

(d) a single stereoisomer

Sol. ***(d)*** S_N2 reaction occurs at asymmetric carbon with inversion in configuration and a single stereoisomer of the product is formed.

Mechanism of S_N1 reaction

Let us consider the following generalised reaction,

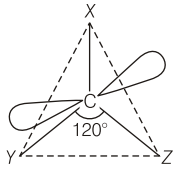


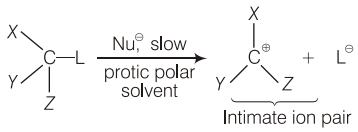
Here, L^- is the leaving group and Nu^- is nucleophile.

X, *Y* and *Z* can be either same or different alkyl groups.

This reaction proceeds stepwise as follows.

Step I The C—L bond is broken due to the presence of nucleophile resulting in the formation of carbocation and L^- instead of short lived transition state. The formation of the carbocation is the rate determining step. A carbocation is an unstable species and so it will be formed slowly from a neutral organic molecule. Ions are developed due to heterolysis.



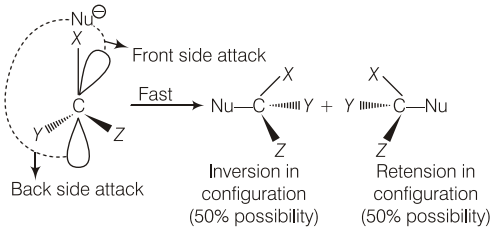


This step involves following changes.

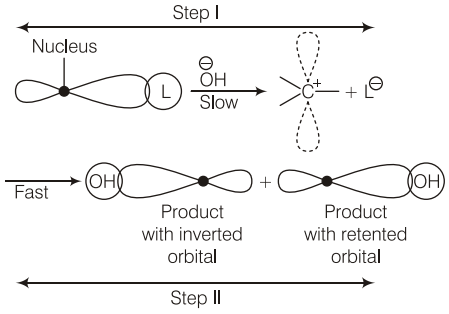
- The bond angle changes from 109°28′ (alkyl halide) to 120° (carbocation).
- The empty orbital present in carbocation is present perpendicular to the plane of alkyl groups attached with carbon atom (as carbocation is sp^2-hybridised).

Step II Once carbocation is formed, being very reactive, all its reactions will be fast regardless of the nature nucleophile.

The nucleophile gives its electrons to empty *p*-orbital by either front side attack or back side attack.



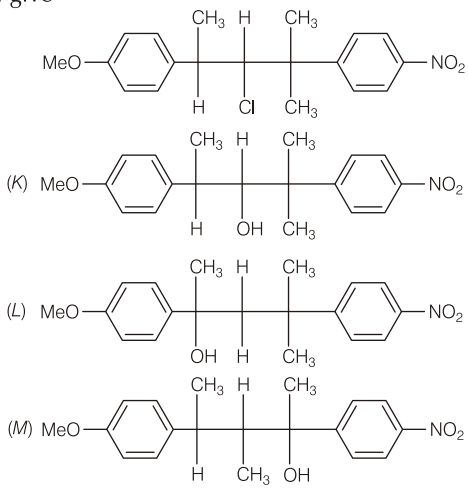
Orbital picture for S_N1 reaction



- The rate determining step, i.e. step-I involves one molecule only, i.e. substrate. Hence, Rate of reaction ∝ [Substrate]
- S_N1 reaction is non-stereospecific and non-stereoselective as attack of nucleophile is not specific and the products are the mixture of enantiomers.

Note
- Stereospecific reactions are those reactions in which stereochemistry of the reactant completely determines the stereochemistry of the product without any other option.
- Stereoselective reactions are those reactions in which there in a choice of pathway, but the product stereoisomer is formed due to its reaction pathway being more favourable than the others available.

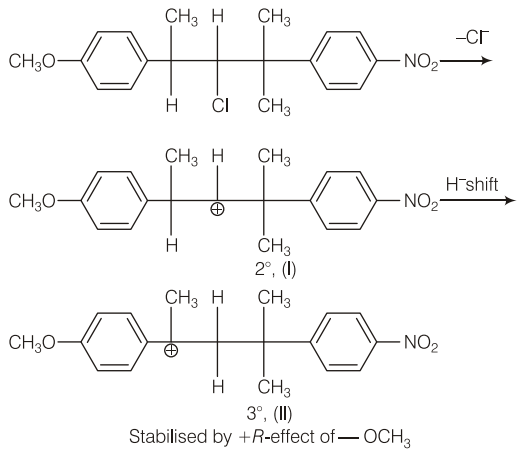
Example 6 The following compound on hydrolysis in aqueous acetone will give



[IIT 2005]

(a) *K* and *L* (b) Only *K* (c) *L* and *M* (d) Only *M*

Sol. **(a)** Reaction proceeds through formation of carbocation intermediate

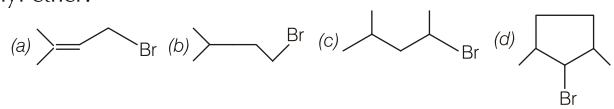


Stabilised by +*R*-effect of — OCH_3

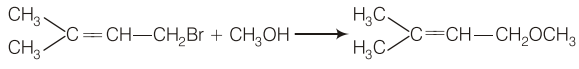
$$I \xrightarrow{H_2O} K$$

$$II \xrightarrow{H_2O} L$$

Example 7 Which one of the following alkyl bromides undergoes most rapid solvolysis in methanol solution to give corresponding methyl ether?



Sol. **(a)** 1-bromo-3-methylbut-2-ene reacts most readily by S_N1 mechanism because the bromine is at allylic position. On the other hand, CH_3OH is a weak nucleophile and weak nucleophile favoures S_N1 mechanism.



SOME KEY POINTS ABOUT S_N1 AND S_N2 MECHANISM

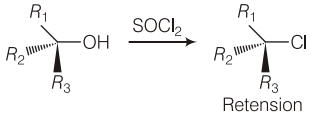
- 2° alcohols can be prepared through either of S_N1 or S_N2 mechanisms.
- Rearrangement of carbocation in order to get more stable carbocation is observed in S_N1 mechanism.
- High concentration of the nucleophile favours S_N2 mechanism while low concentration of nucleophile favours S_N1 mechanism For e.g. $(CH_3)_3CCH_2Br$ shows S_N2 mechanism with $C_2H_5O^-$ but S_N1 mechanism with C_2H_5OH.

S_Ni Reaction (Internal nucleophilic substitution reaction)

- In this reaction, no real carbocation is formed, which leads to racemisation.
- This reaction occurs when the initial attack of nucleophile produces cyclic intermediate or an intermediate complex with tight ion pairing.
- In this reaction neighbouring group participation occurs.
- This reaction explains the non-inversion or retention in stereochemical configuration of products in many cases.
- The organic reaction shows this mechanism in the chlorination of alcohols with thionyl chloride.

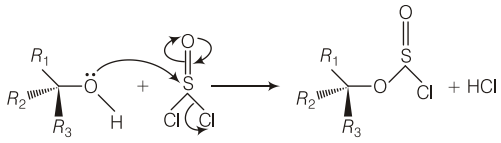
Mechanism of S_Ni Reaction

Let us consider the following generalised reaction.

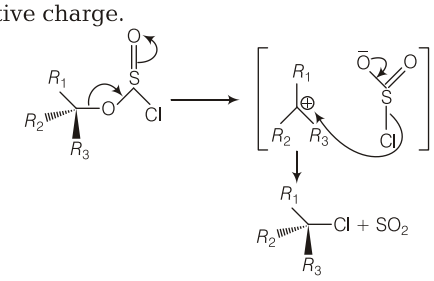


This reaction proceeds stepwise as follows

***Step* I** Alcohol first reacts with thionyl chloride and forms alkyl chloro sulphite.



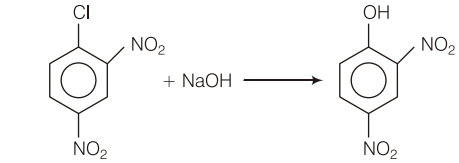
***Step* II** Sulphur dioxide is lost from alkyl chloro sulphite and chloride ion is attached to carbon atom bearing positive charge.



The carbocation gets complexed before it is racemised. Hence, stereochemical integrity is maintained.

Nucleophilic Substitution Reaction in Haloarenes (S_NAR reactions)

- Aryl halides undergo nucleophilic substitution with extreme difficulty.
- However, aryl halides undergo nucleophilic substitution readily, if the aromatic ring contains, in addition to halogen, certain other properly placed groups: electron withdrawing groups (EWGs) like $—NO_2$, —NO, —CHO or —CN, located at *ortho* or *para*-position to the halogen.
- The EWGs weakens the strength of C—*X* bond by withdrawing electrons from benzene ring which results ease of removal of halide ion by a strong nucleophile.
- Some examples are given below.

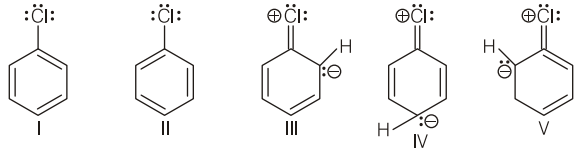


Here, $\bar{O}H$ acts as nucleophile.

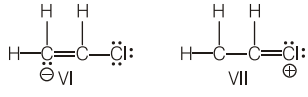
- However, electron donating groups at *ortho* or *para*-position makes C—*X* bond stronger because these groups increase the electron density within the aromatic ring which results in the development of double bond character in C—*X* bond. Thus, a nucleophilic substitution reaction occurs with extreme high difficulty.

Reason of Low Reactivity of Aryl and Vinyl Halides

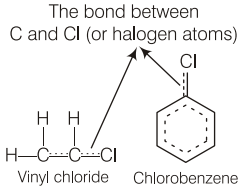
- The low reactivity of aryl and vinyl halides towards nucleophilic substitution reactions has been attributed due to two factors.
  - (i) Delocalisation of electrons by resonance.
  - (ii) Difference in σ bond energies due to difference in hybridisations of carbon.
- Chlorobenzene is considered to be a hybrid of not only the two Kekule structures I and II, but also of three structures III, IV and V, in which chlorine is attached to carbon by a double bond, in III, IV and V chlorine bears a positive charge and the *ortho* and *para*-positions of ring bear a negative charge.



- Similarly, vinyl chloride is considered to be a hybrid structure of VI and VII.

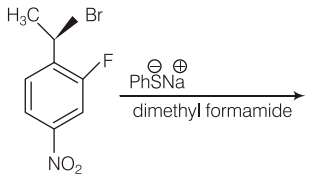


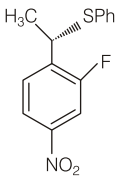
- Contribution from III, IV and V; and from VII stabilises the chlorobenzene and vinyl chloride molecules respectively and gives double bond character to the carbon-chlorine bond.

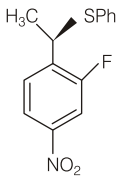


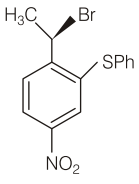
- Thus, carbon and chlorine are held together by something more than a single pair of electrons, and the carbon-chlorine bond is stronger than it was in a pure single bond.

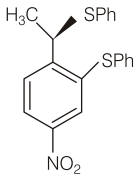
Example 8 The major product of the following reaction is [IIT 2008]



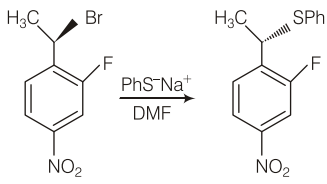
(a) 

(b) 

(c) 

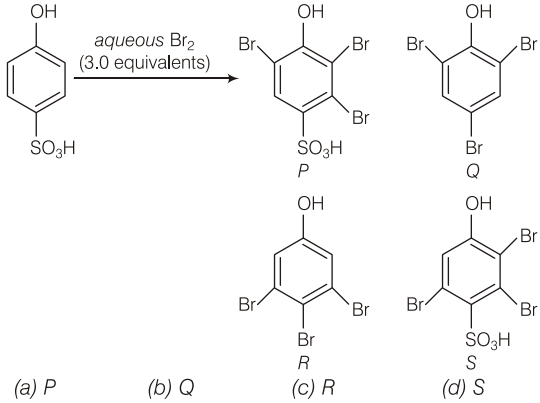
(d) 

Sol. **(a)**



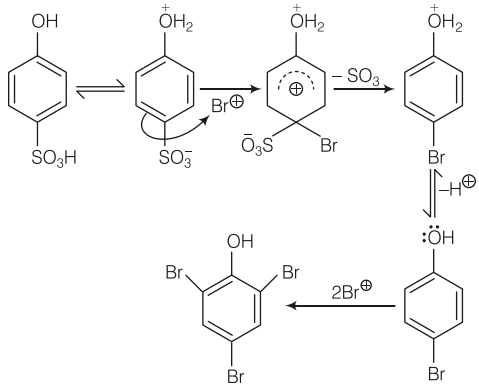
S_N2 reaction brings about inversion of configuration.

Example 9 The major product(s) of the following reaction is (are) [JEE Advanced 2013]



(a) P (b) Q (c) R (d) S

Sol. **(b)** —OH group is activating group and is *o*-and *p*-directing. Also —SO_3H is a better leaving group and knocked out by Br^-.



Example 10 The compound that will react most readily with NaOH to form methanol is [IIT 2009]

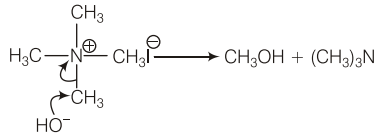
(a) $(CH_3)_4\overset{+}{N}\overset{-}{I}$

(b) CH_3OCH_3

(c) $(CH_3)_3\overset{+}{S}\overset{-}{I}$

(d) $(CH_3)_3CCl$

Sol. **(a)**



Lack of β-hydrogen on quaternary ammonium iodide, leads to S_N2 reaction otherwise E-2 elimination usually takes place.

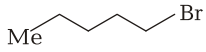
AMAZING REALITIES

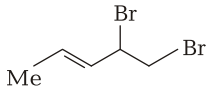
The muscles of fishes contain a substance called trimethylamine oxide (TMAO) which is broken down by decomposition. The result is trimethylamine and dimethylamine. The mixing of these two amines results in that characteristic fishy smell. In fact, it is the presence of trimethylamine that is used as an indicator of how fresh a fish is.

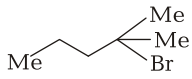
Smart Practice

Single Option Correct Type

1. Which one of the following halides will be most reactive for S_N2 and S_N1 reaction, respectively?

I. 

II. 

III. 

(a) I and II *(b)* II and I *(c)* I and III *(d)* Only III

2. $Ph—CH(OH)CH_3 \xrightarrow{SOCl_2} Ph—\underset{\displaystyle Cl}{\underset{|}{CH}}—CH_3$

by which of the following mechanism does the above reaction proceed?

(a) S_N1 *(b)* S_N2 *(c)* S_Ni *(d)* E-2

3. Which one of the following alkyl halides undergoes S_N1 reaction fastest?

(a) Methyl chloride *(b)* Ethyl chloride
(c) *Iso*-butyl chloride *(d)* *Tert*-butyl alcohol

4. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to

(a) the formation of less stable carbocation
(b) resonance stabilisation
(c) larger carbon-halogen bond
(d) inductive effect

5. $CH_3Br + Nu^- \longrightarrow CH_3—Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophile (Nu^-) *A* to *D* is

[Nu = (*A*) PhO^-, (*B*) ACO^-, (*C*) HO^-, (*D*) CH_3O^-]

(a) *D* > *C* > *A* > *B* *(b)* *D* > *C* > *B* > *A*
(c) *A* > *B* > *C* > *D* *(d)* *B* > *D* > *C* > *A*

6. What is the correct increasing order of reactivity of the following in S_N2 reaction?

I. $CH_2=CH—CH_2—Br$
II. $CH_2=CH—I$
III. $CH_3CH_2CH_2—I$
IV. $CH_3OCH_2CH_2I$

(a) I<II<III<IV *(b)* III<II<I<IV
(c) II < III < IV < I *(d)* II < I < III < IV

7. What is the correct increasing order of reactivity of the following in the S_N2 reaction?

I. $(CH_3)_3CCH_2Cl$ II. $CH_3CH_2CH(Cl)CH_3$
III. C_6H_5Cl IV. *p*-$NO_2-C_6H_4CH_2Cl$

(a) I<II<III<IV *(b)* III<II<I<IV
(c) II<III<IV<I *(d)* III<I<II<IV

8. The correct statement regarding a S_N2 reaction is

(a) the reaction mechanism involves atleast one reactive intermediate
(b) transition state is pentavalent
(c) product is formed after passing through several transition states
(d) nucleophile attacks from front side on which leaving group is present

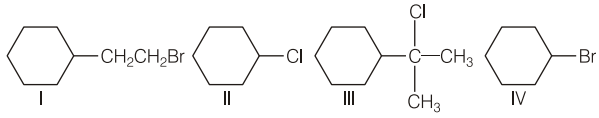
9. A correct statement about transition state of S_N2 reaction is

(a) the transition state proceeds and follow an unstable reaction intermediate
(b) the transition state will always have net negative charge
(c) existence of this state implies that S_N2 reaction is an exothermic reaction
(d) the single transition state represents the point of maximum free energy of the reaction

10. Which of the following would be the strongest nucleophile in methanol?

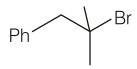
(a) $\bar{O}H$ *(b)* $\bar{S}H$ *(c)* $\bar{S}eH$ *(d)* $\bar{T}eH$

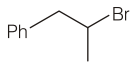
11. Arrange the following in increasing order of reactivity in an S_N2 reaction with KI in acetone solvent.

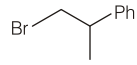


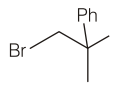
(a) I<IV<III<II *(b)* IV<I<III<II *(c)* II<III<I<IV *(d)* III<II<I<IV

12. Which of the following is the most reactive alkyl halide for an S_N1 reaction?

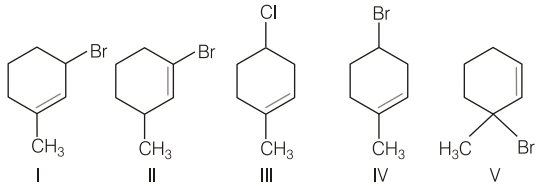
(a) 

(b) 

(c) 

(d) 

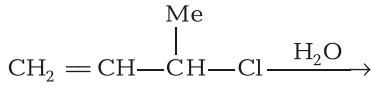
13. Rank the following molecules in increasing order of relative rate of S_N1 solvolysis with methanol and heat.



(a) III<II<IV<V<I *(b)* II<III<IV<I<V
(c) V<IV<III<II<I *(d)* II<III<IV<V<I

More than One Correct Type

14. Consider the following reaction.



Choose the correct statement.

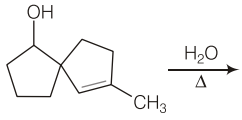
(a) The product is major

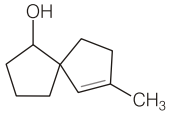
(b) The product is a mixture of and HO—CH_2—CH = CH—Me

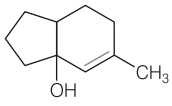
(c) Allyl chloride gives S_N2 reaction

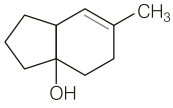
(d) Formation of HO—CH_2—CH = CH—Me takes place by an allylic mechanism.

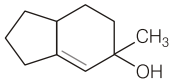
15. What is/are the expected solvolysis product(s) in the following reaction?



(a) 

(b) 

(c) 

(d) 

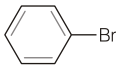
16. Consider the following S_N2 reaction 1-bromo- butane + NaCN(*aq*) → pentane-1-nitrite + NaBr. Which of the following solvent (s) when replaces water in the above reaction increases the rate?

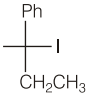
(a) Acetone (b) Dimethyl sulphoxide
(c) N,N-dimethyl formamide (d) Tetrahydrofuran

17. 1-Chlorobutane is more reactive than 2-chloro-2-methyl-1-propane in a S_N1 reaction because

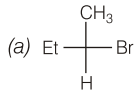
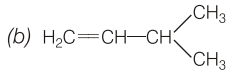
(a) α-carbon is less crowded in 1-chlorobutane
(b) α-carbon is less electropositive in 1-chlorobutane
(c) electron donating inductive effect of three methyl groups is greater in-2-chloromethyl propane
(d) α-carbon is more electropositive in 1-chlorobutane

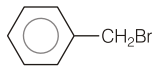
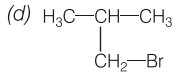
18. Which of the following compounds will give S_N1 reaction?

(a) $H_3C—CH_2—Br$ (b) 

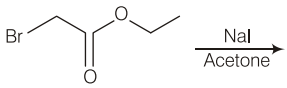
(c) $H_3C—\ddot{O}—CH_2—Cl$ (d) 

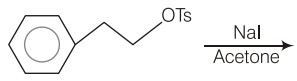
19. Which of the following compounds will give racemic mixture by S_N1 reaction?

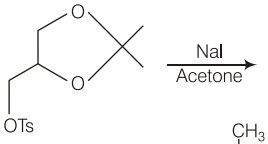
(a)  (b) 

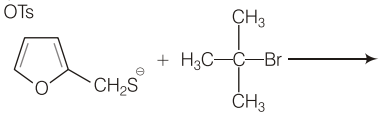
(c)  (d) 

20. Which of the following reactions take place by S_N2 mechanism?

(a) 

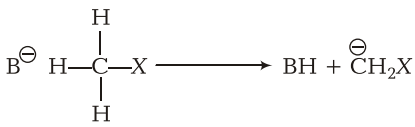
(b) 

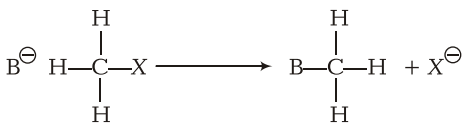
(c) 

(d) 

Paragraph Type Question

The rate of S_N2 reaction depends on the effectiveness of the nucleophile in ejecting the leaving group. Nucleophilicity is the affinity for C-atom, while basicity is the affinity for proton.





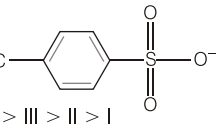
In both cases, a new bond is formed. If a new bond is formed between the anion and proton, the species acts as a base. If a new bond is formed between the anion and C-atom, the species acts as an nucleophile.

21. Which one of the following statement is wrong?

(a) The nucleophilicity order of halides in CCl_4 is $I^- > Br^- > Cl^- > F^-$
(b) The nucleophilicity order of halides in H_2O is $I^- > Br^- > Cl^- > F^-$
(c) The nucleophilicity order of halides in acetone is $F^- > Cl^- > Br^- > I^-$
(d) The nucleophilicity order of halides in DMSO is $F^- > Cl^- > Br^- > I^-$

22. The decreasing order of nucleophilicity among the following nucleophiles is

I. $CH_3-\underset{\underset{O}{\|}}{C}-O^-$ II. CH_3O^-

III. CN^- IV. 

(a) I > II > III > IV *(b)* IV > III > II > I

(c) II > III > I > IV *(d)* III > II > I > IV

In an S_N2 reaction, hydroxylic solvents like water, alcohol, carboxylic acid etc, solvate nucleophile and decreases its reactivity in the reaction. Size of donor atom of nucleophile also affect nucleophilicity. A larger donor atom is more easily polarised and less solvated, hence a stronger nucleophile.

23. Which of the following describes correctly the role of H_2O as a solvent in an S_N2 reaction?

(a) It stabilises nucleophile but not transition state

(b) It stabilises transition state but not nucleophile

(c) It stabilises both transition state and nucleophile but greater extent to nucleophile

(d) It stabilises both transition state and nucleophile but greater extent to transition state.

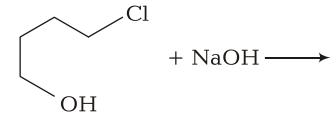
24. In water, the order of nucleophilicity of halides is

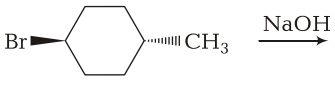
(a) $I^- < Br^- < Cl^- < F^-$ *(b)* $F^- < Cl^- < Br^- < I^-$

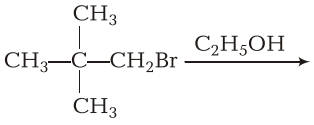
(c) $I^- = Br^- = Cl^- = F^-$ *(d)* $F^- = Cl^- < Br^- < I^-$

Integer Type Questions

25. How many of the following reactions go through S_N2 mechanisms?

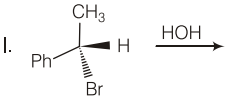
I. 

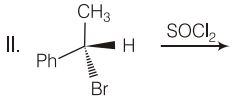
II. 

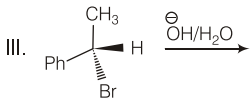
III. 

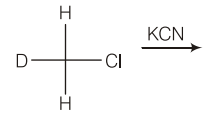
IV. $CH_3CH_2CH_2CH_2Br + KCN \longrightarrow$

26. Find out the number of reactions those proceed with retention of configuration?

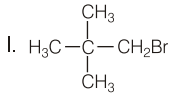
I. 

II. 

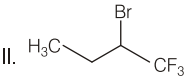
III. 

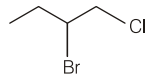
IV. 

27. Under identical experimental conditions, how many of the following substrates react at faster rate with aqueous NaOH than 2-bromobutane as substrate?

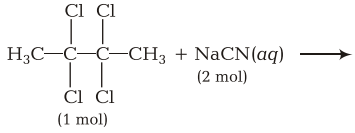
I. 

II. $CH_3CH_2CH_2CH_2Cl$

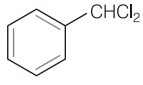
III. 

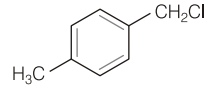
IV. 

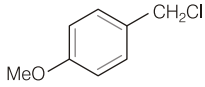
28. In the following reaction. How many different types of dicyano products are expected?

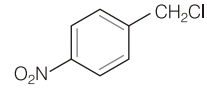


29. How many of the following undergo S_N1 reactions faster than benzyl chloride?

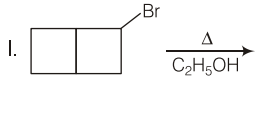
I. 

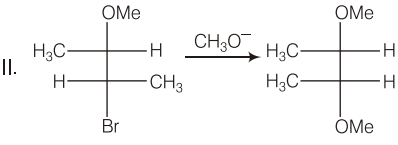
II. 

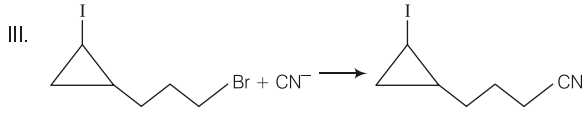
III. 

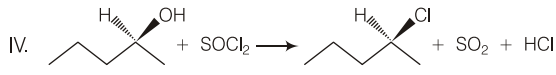
IV. 

30. How many of the following reaction(s) is/are correct?

I. 

II. 

III. 

IV. 

Answers

1. (c)	**2.** (c)	**3.** (d)	**4.** (b)	**5.** (a)	**6.** (c)	**7.** (d)	**8.** (b)	**9.** (d)	**10.** (d)
11. (b)	**12.** (a)	**13.** (b)	**14.** (b,c,d)	**15.** (a,b,d)	**16.** (c,d)	**17.** (a,c,d)	**18.** (c,d)	**19.** (a,b)	**20.** (a,b,c)
21. (c)	**22.** (c)	**23.** (c)	**24.** (b)	**25.** (3)	**26.** (3)	**27.** (3)	**28.** (4)	**29.** (2)	**30.** (4)

[Elements : Iron and Copper]

We have read some interesting things like discoveries and properties of silver and gold in July issue. In this issue we shall discuss about copper and iron. Copper and iron both are metals, thus are good conductors of heat and electricity. Today, these metals are widely used in electronics, medicine, building constructions, jewellery, farming, security systems etc. We are going to discuss about these two elements one-by-one. Lets start with copper.

Copper

- Copper beads have been excavated in northern Iraq which are atleast 11000 yr old. Thus, people have been using copper for atleast 11000 yrs.
- The Roman Empire obtained most of its copper from the Island of Cyprus, from where copper name originated.
- At first people used only native copper but later rising demand led to the processing of copper ores. It is comparatively simple to smelt the metal from ores with higher copper content.
- Pure copper was usually too soft for most uses. Hence, copper was widely used in the ancient world as bronze (an alloy of copper with tin), which was used to make cultery coins and tools. In China, it was used for bells. The alloy, bronze marked a whole epoch in the history of mankind the Bronze Age.
- As early as the third millenium BC copper was widely used for manufacturing various tools. The Egyptian Pyramid of cheops was built with gigantic stone blocks each of which was cut with copper tools.
- At first bronze was rather expensive and was used mainly for jewellery and luxury articles. In ancient Egypt, mirrors were made from bronze. Bronze, like copper, proved to be an excellent material for relict makers and sculptors.
- As early as the 5th century BC man learned to cost bronze statues.
- Besides bronze another wonderful copper alloy, brass, has been known for a long time. It was prepared by fusing copper with zinc ore. Ancient Egyptians, Indians, Assyrians, Romans, and Greeks knew copper, bronze and brass. Both copper and bronze were used for making weapons. In excavations dated back to the 8th-6th centuries BC in Altai, Siberia, and *trans*-caucasus archaeologists found knives, arrow-heads, shields, and helmets made from bronze and copper.
- Today, copper is mainly obtained from the ores cuprite(CuO_2), tenorite (CuO), malachite ($CuO_3 \cdot Cu(OH)_2$), chalcocite (Cu_2S), covellite (CuS) and bornite (Cu_5FeS_4). Large deposits of copper ore are all located in six Intergovernmental Council of Copper Exporting Countries : United States, Chile, Zambia, Zairu, Peru and Canada formed in 1967.
- Copper is used in large amount by the electrical industry in the form of wire, copper is second only to silver in electrical conductor.
- Today copper has many applications in different fields such as in organometallic chemistry, architecture, medicine, making of wires, cables, electronics and related devices, electric motors (copper superior conductivity enhances the efficiency of electrical motors).
- Copper proteins have diverse roles in biological electron transport and oxygen transportation processes that exploit the easy interconversion of Cu (I) and Cu (II). The biological role of copper commenced with the appearance of oxygen in earth's atmosphere.

Iron

- Iron objects have been found in Egypt dating from around 3500 BC. They contain about 7.5% nickel, which indicates that they were of meteoric origin.
- Iron is the second most abundant metal in nature after aluminium.
- A chemical symbol Fe originates from the latin word *ferrum*, which means 'iron'.
- Native iron is extremely rare because it oxidises readily in the presence of water and air and is found mainly in the form of oxides.
- In the beginning, iron was very expensive and was valued much higher than gold; very often iron jewellery was set in gold. This is because, peoples of all continents became aware of gold, silver and copper approximately at the same time. But in the case of iron this awareness comes at different timings.
- In Egypt and Mesopotamia the process of extracting iron from ores was discovered 2000 BC; in *trans*-caucasus, Asia Minor, and ancient Greece at the end of the second millenium; in India in the the middle of the second millenium in China much later, only in the middle of the first millenium BC.
- The New World Iron Age (1300-1200 BC) began with the arrival of Europeans, i.e. in the second millenium AD; some African tribes began to use iron skipping the Bronze Age period.
- In countries where natural resources of copper and tin were small, a demand arose for replacing these metals.
- Gradually, production of iron grew and iron began to pass from the category of precious metals into the ordinary ones.
- Among all the metals and alloys known by the time, iron was the hardest one. Therefore, as soon as iron grew relatively cheap, various tools and weapons were manufactured from it.
- At the beginning of the first millenium AD, production of iron in Europe and Asia had made considerable progress; particularly great success in smelting and processing iron had been achieved by Indian metallurgists.
- By the end of the 15th century first smelting furnaces appeared producing exclusively cast iron.
- Today, one third of Earth's mass in believed to be iron, most of which lies deep within the planet, i.e. in the core.
- You may be surprised after knowing that there is enough iron present on Earth to make three new planets, each with the same mass as Mars.

30 Best One or More than One Correct Type Problems On THE GASEOUS STATE

A collection of chapterwise best problems of their types

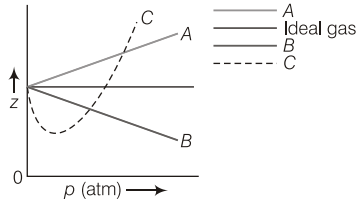
1. According to the kinetic theory of gases **[2011 adv]**

(a) collisions are always elastic
(b) heavier molecules transfer more momentum to the wall of the container
(c) only a small number of molecules have very high velocity
(d) between collisions, the molecules move in straight lines with constant velocities

2. A gas described by van der Waals' equation **[2008 adv]**

(a) behaves similar to an ideal gas in the limit of large molar volumes
(b) behaves similar to an ideal gas in the limit of large pressures
(c) is characterised by van der Waals' coefficient that are dependent on the identity of the gas but are independent of the temperature
(d) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

3. The given graph represent the variations of Z (compressibility factor $(Z) = \frac{pV}{nRT}$) *versus* p, for three real gases A, B and C. Identify the only incorrect statement. **[2006 adv]**



(a) For the gas A, $a = 0$ and its dependence on p is linear at all pressure
(b) For the gas B, $b = 0$ and its dependence on p is linear at all pressure
(c) For the gas C, which is typical real gas for which neither a nor $b = 0$. By knowing the minima and the point of intersection, with $Z = 1$, a and b can be calculated
(d) At high pressure, the slope is positive for all real gases

4. At sea level, the composition of dry air is approximately $N_2 = 75.5\ \%$, $O_2 = 23.2\ \%$ and $Ar = 1.3\ \%$ by mass. If the total pressure at the sea level is 1 bar, which of the following option(s) is/are correct?

(a) Partial pressure of N_2 is greater than that of O_2
(b) Argon gas has the least partial pressure among N_2, O_2 and Ar
(c) Partial pressure of N_2 is less than that of O_2
(d) All the gases have same partial pressure

5. According to Graham's law of diffusion/effusion, under similar conditions of temperature and pressure

(a) the rate of diffusion of different gases are inversely proportional to the square roots of their corresponding densities
(b) the rates of diffusion of gases are directly proportional to their molecular masses
(c) the rates of diffusion of gases are inversely proportional to their molecular masses
(d) the rates of diffusion of different gases are directly proportional to the square roots of their density

6. At very high pressure the van der Waals' equation reduces to

(a) $pV = RT - \frac{a}{V}$ *(b)* $p = \frac{RT}{V - b}$
(c) $pV = \frac{aRT}{V^2}$ *(d)* $pV = RT + pb$

7. There are four sets of rings of safety valve of a pressure cooker as 5 L, 10 L and 25 L per square inch. If a piece of chicken to be cooked at a temperature of 160°C, to what pressure should the valve be set? (The cooker is sealed with dry air at NTP)

(a) 25 lb *(b)* 24 lb *(c)* 21 lb *(d)* 22 lb

8. A spherical air bubble is rising from the depth of a lake when pressure is p atm and temperature is TK. The percentage increase in its radius when it comes to the surface of a lake will be (Assume temperature and pressure at the surface to be $2T$ K and $p/4$, respectively).

(a) 100% *(b)* 50% *(c)* 40% *(d)* 200%

9. Which of the following statements is/are correct?

(a) The difference between the rms speed and the mean speed at any temperature for different gases diminishes as larger, and yet larger molar masses are considered

(b) Mean kinetic energy of the gas molecules at any given temperature is independent of the mean speed

(c) The ratio of the mean speed to the rms speed is independent of the temperature

(d) The square of the mean speed of the molecules is equal to the square of the rms speed at a certain temperature

10. The characteristics of a real gas are

(a) it obeys gas laws only at very low pressures and high temperatures

(b) the volume of molecules of real gas is negligible

(c) a real gas does not have attractive forces among its molecules at high pressures and low temperature

(d) it satisfies van der Waals' equation

11. If two gases have the same value of a but different values of b (a and b are van der Waals' constant), then

(a) the gas having a smaller value of b will occupy lesser volume

(b) the gas having a smaller value of b has larger compressibility

(c) the gas having a smaller value of b has lesser compressibility

(d) Both (a) and (b)

12. What percentage of a sample of nitrogen must be allowed to escape if its temperature, pressure and volume are changed from 220°C, 3 atm and 1.65 L to 110°C, 0.7 atm and 1.0 L, respectively.

(a) 92.71 *(b)* 80.21 *(c)* 81.87 *(d)* 100.12

13. The density of the vapour of a substance at 1atm pressure and 500K is 0.36 kgm^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition. Which of the following option(s) is/are correct?

(a) The molecular mass of a substance is 18.09 g mol^{-1}

(b) The molar volume of the vapour is 50.25 dm^3mol^{-1}

(c) The compressibility factor is 1.22

(d) The attractive forces dominate among the gaseous molecules

14. A gas bulb of 1L capacity contains 2.0×10^{15} molecules of nitrogen exerting a pressure of $7.57\times10^{-3}Nm^{-2}$. The ratio of the most probable speed to the root mean square speed is 0.82.

Which of the following statements is/are correct?

(a) The most probable velocity of molecules is 404.45 ms^{-1}

(b) Temperature inside the bulb is 273.15K

(c) The root mean square velocity of molecules is 493.27 ms^{-1}

(d) All of the above

15. A helium atoms is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is

(a) two times that of a hydrogen molecule

(b) four times that of a hydrogen molecule

(c) half that of a hydrogen molecule

(d) same as that of a hydrogen molecule

16. The compression factor for 1 mole of van der Waals' gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible calculate the van der Waals' constant 'a' in L^2 mol^{-2} atm.

(a) 1.021 *(b)* 0.871 *(c)* 1.253 *(d)* 0.792

17. At 27°C hydrogen is leaked through a tiny hole into a vessel for 20 min. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for 20 min. After the effusion of the gases, the mixture exerts a pressure of 6 atm. The hydrogen content of the mixture is 0.7 mole and volume of the container is 3L

Which of the following statements is/are correct?

(a) The mass of unknown gas in the mixture is 21.9 g

(b) The number of moles of unknown gas in the mixture is 0.0308 mol

(c) The molecular mass of unknown gas in the mixture is 1033 g mol^{-1}

(d) All of the above

18. At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to

(a) increase in average molecular speed

(b) increase in number of mole

(c) increase in molecular attraction

(d) decrease in mean free path

19. Which of the following statement(s) is/are true about the effect of an increase in temperature on the distribution of molecular speeds in a gas?

(a) The area under the distribution curve remains the same as under the lower temperature

(b) The distribution becomes broader

(c) The fraction of the molecules with the most probable speed increases

(d) The most probable speed increases

20. Two bulbs A and B of same capacity are filled with He and SO_2 respectively, at the same temperature.

(a) The ratio of u_{rms} for He to SO_2 is 4:1

(b) At 1200 K, speed of SO_2 becomes half of the speed of He molecules at 27°C

(c) If volume of B becomes four times, root mean square speed of molecules gets slower
(d) If half of the molecules of SO_2 are removed from B root mean square speed of molecules gets faster

21. Which of the following statements is/are correct for real gas?
(a) $Z > 1$ means that it is more difficult to compress the real gas in comparison to the ideal gas
(b) $Z < 1$, means that it is easy to compress the real gas in comparison to the ideal gas
(c) $Z > 1$, means that repulsive forces are dominating among gaseous species
(d) $Z < 1$, means that attractive forces are dominating among gaseous species

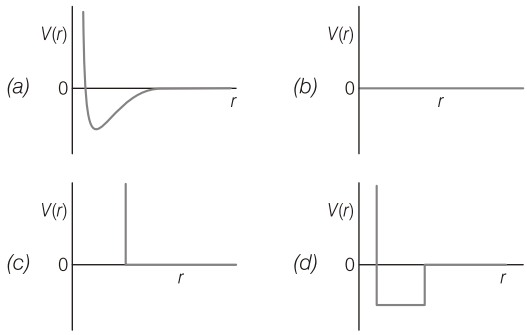
22. Which of the following options is/are correct for real gas?
(a) At very low pressure: $pV \approx nRT$
(b) At low pressure: $pV < RT$
(c) At average pressure: $pV \approx RT$
(d) At high pressure: $pV < RT$

23. Which of the following statement(s) is/are correct for Dalton's law?
(a) It is used to calculate pressure of gas collected over water
(b) It is used to calculate percentage of gas in a mixture
(c) This law is applicable for gaseous components which react with each other
(d) It is used to calculate relative humidity (R_H) at a given temperature

24. An LPG (liquified petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weights 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the weight of the full cylinder reduces to 23.2 kg. (Assume LPG to the n-butane with normal boiling point of 0°C). Which of the following statements is/are correct?
(a) The volume of the gas used up is 2.46 m^3
(b) The change in pressure of the gas inside the cylinder is 1.50 atm
(c) The final pressure inside the cylinder is 1.50 atm
(d) The mass of remaining gas after used up is 8.4 kg

25. The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2Cl$), which is attained at 1200°C, is determined by measuring the rate of effusion through a pinhole. It is observed that at 1.80 mm of Hg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. (Atomic mass of krypton = 84)
(a) 12.4 % (b) 14.0 %
(c) 13.0 % (d) 14.9 %

26. One mole of a monoatomic real gas satisfies the equation $p(V - b) = RT$ where, b is a constant. The relationship of interatomic potential $V(r)$ and interatomic distance r for gas is given by
[JEE (Adv.) 2015]



27. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases X times. The value of X is
[JEE (Adv.) 2016]
(a) 1 (b) 2 (c) 3 (d) 4

28. Which one of the following statements is/are incorrect?
(a) To avoid bumping of stopper, the closed bottle of $NH_3(l)$ should be cooled
(b) The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is Boyle temperature
(c) A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal potential energy
(d) Rate of diffusion of a gas is directly proportional to the square root of its molecular weight

29. At 400K, the root mean square (rms) speed of a gas X (Molecular mass = 40 g mol^{-1}) is equal to the most probable speed of Y at 60K. The molecular mass of the gas Y is **[JEE (adv.) 2009]**
(a) 8 g mol^{-1} (b) 12 g mol^{-1}
(c) 4 g mol^{-1} (d) 2 g mol^{-1}

30. Using van der Waals' equation, calculate the constant 'a' in the units of atm $L^2 mol^{-2}$ when two moles of a gas confined in four litre flask exert a pressure of 11.0 atm at a temperature of 300K. The value of 'b' is 0.05 L mol^{-1}.
(a) 9.79 (b) 8.42
(c) 5.29 (d) 6.46

AMAZING REALITIES

The Chinese accidentally discovered that a mixture of sulphur, charcoal and potassium nitrate burnt quickly with a big flash. Excited by this wonderful sight, they filled the mixture into bamboo shoots and threw them into the fire. The green bamboo shoots exploded making a large sound. And thus, fireworks were born.

Answers with Explanation

1. ***(a,c,d)*** Kinetic energy is given as,

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m} \quad \ldots (i)$$

But we also know that kinetic energy for a molecule,

$$KE = \frac{3}{2}kT \quad \ldots (ii)$$

From (i) and (ii) $\frac{p^2}{2m} = \frac{3}{2}kT$

or $p^2 = 3mkT$

i.e. $p \propto \sqrt{m}$

Hence, heavier molecules will transfer more momentum to the wall of the container.

But this is not the postulate of kinetic theory of gases.

2. ***(a,c)*** Option (b) is incorrect because in the limit of large pressures, compressibility factor $(Z) > 1$.

i.e. $\frac{pV}{RT} > 1$

Option (d) is incorrect because Z can either less or greater than unity hence, real pressure can be less or greater than ideal pressure.

3. ***(b)*** At high pressure slope of the line will change from negative to positive.

4. ***(a,b)*** As composition is given in percentage, so let us consider the mass of dry air is equal to 100g.

Now, moles of

$$N_2(n_{N_2}) = \frac{75.5\text{ g}}{28\text{ g mol}^{-1}} = 2.7 \text{ moles}$$

$$\left(\text{Number of moles} = \frac{\text{Mass (in g)}}{\text{Molar mass (g mol}^{-1})}\right)$$

Similarly, moles of

$$O_2(n_{O_2}) = \frac{23.2\text{g}}{32\text{ g mol}^{-1}} = 0.725 \text{ mol}$$

Moles of $Ar(n_{Ar}) = \frac{1.3\text{ g}}{40\text{g mol}^{-1}} = 0.0325$ mol

Total moles of all three gases

$= (2.7 + 0.725 + 0.0325)$ moles

$= 3.4575$ moles

Mole fraction of $N_2(\chi_{N_2}) = \frac{2.7}{3.4575} = 0.781$ of air

$$\left(\text{Molar fraction} = \frac{\text{Moles of one constituent gas}}{\text{Total moles of all gases}}\right)$$

Similarly,

Mole fraction of $O_2(\chi_{O_2}) = \frac{0.725}{3.4575} = 0.209$

Mole fraction of $Ar(\chi_{Ar}) = \frac{0.0325}{3.4575} = 9.4 \times 10^{-3}$

Hence, partial pressure of

$N_2(p_{N_2}) = p_{total} \times \chi_{N_2} = 1 \times 0.781 = 0.781$ bar

partial pressure of

$O_2(p_{O_2}) = p_{total} \times \chi_{O_2} = 1 \times 0.209 = 0.209$ bar

partial pressure of

$Ar(p_{Ar}) = p_{total} \times \chi_{Ar} = 1 \times 9.4 \times 10^{-3}$

$= 9.4 \times 10^{-3}$ bar

Thus, according to the above data, option (a) and option (b) are correct.

5. ***(a,c)***

6. ***(b, d)*** $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$

At high pressure $p >> \frac{an^2}{V^2}$

$p(V - nb) = nRT$

$p = \frac{nRT}{V - nb}$

For $n = 1$ $p = \frac{RT}{V - b}$

also, $pV - pb = RT$

$pV = RT + pb$

7. ***(b)*** Key Concept *According to Gay Lussac's law, at constant volume, pressure of a gas ∝ temperature*

or $\frac{p}{T} = constant$

At two different temperatures

$\frac{p_1}{T_1} = \frac{p_2}{T_2}$

$p_1 = 760$ mm of Hg (At 273 K)

$= 14.7$ lb / sq·inch

$T_1 = 273K, T_2 = (160 + 273)K = 433$ K

Now, $p_2 = p_1 \times \frac{T_2}{T_1} = \frac{14.7 \times 433}{273} = 23.3$ lb / sq· inch

At 160°C, the pressure of air would be 23.31 lb / sq· inch. Hence, valve should be set at 24 lb/sq.inch.

8. ***(a)*** $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$\frac{pV_1}{T} = \frac{p}{4} \times \frac{V_2}{2T}$

$V_1 = \frac{V_2}{8}$

$\therefore$ $V_2 = 8V_1 = 8 \times \frac{4}{3}\pi r^3$ $\left[\because \text{Volume of sphere} = \frac{4}{3}\pi r^3\right]$

$= \frac{4}{3}\pi(2r)^3$

New radius $= 2r$

$\therefore$ 100% radius will increase.

9. ***(a,b,c)*** $v_{av} = \sqrt{\frac{8RT}{\pi M}}$ and $v_{rms} = \sqrt{\frac{3RT}{M}}$

On squaring both terms we get,

$v_{av}^2 = \frac{8RT}{\pi M}$ and $v_{rms}^2 = \frac{3RT}{M}$

Hence, v_{av}^2 is not equal to v_{rms}^2.

10. ***(a,d)***

11. ***(c)*** For smaller value of b, volume correction $(V - nb)$ comes out to be larger. Thus, molecules will show considerable volume which results in lesser compressibility.

12. ***(c)*** Applying the formula,

$$m \text{ (mass of the gas)} = \frac{pV \times M}{RT}$$

$$\text{Mass of gas before escaping} = \frac{3 \times 1.65 \times 28}{0.0821 \times 493} = 3.42 \text{ g}$$

$$\text{Mass of gas after escaping} = \frac{0.7 \times 1.0 \times 28}{0.0821 \times 383} = 0.62 \text{ g}$$

Percentage of nitrogen allowed to escape

$$= \frac{(3.42 - 0.62)}{3.42} \times 100 = 81.87$$

13. ***(a,b,c)*** According to the Graham's law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{1.33}{1} = \sqrt{\frac{32 \text{ g mol}^{-1}}{M_1}}$$

$$\Rightarrow \qquad M_1 = 18.09 \text{ g mol}^{-1}$$

The molar volume of the vapour is

$$V_{real} = \frac{M_1}{d} = \frac{18.09 \text{ g mol}^{-1}}{0.36 \text{ kg m}^{-3}}$$

$$= 50.25 \text{ dm}^3 \text{ mol}^{-1}$$

The compressibility factor (Z) is

$$Z = \frac{V_{real}}{V_{ideal}} = \frac{V_{real}}{(RT)/p} = \frac{pV_{real}}{RT}$$

$$= \frac{(101.325 \text{ kPa})(50.25 \text{ dm}^3\text{mol}^{-1})}{(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(500 \text{ K})}$$

$$= 1.22$$

Since $Z > 1$, the repulsive forces dominate among the gaseous molecules.

14. ***(d)*** The root mean square is given as,

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

In order to calculate v_{rms}, first we have to calculate temperature (T).

From gaseous law, $pV = nRT$

$$T = \frac{pV}{nR} = \frac{7.57 \times 10^{-3} \times 1 \times 10^{-3}}{\frac{2.0 \times 10^{15}}{6 \times 10^{23}} \times 8.314} = 273.15\text{K}$$

$$\therefore \qquad v_{rms} = \sqrt{\frac{3 \times 8.314 \times 273.15}{28 \times 10^{-3}}} = 493.27 \text{ ms}^{-1}$$

$\therefore$ Most probable velocity

$$v_{mp} = 0.82 \times 493.27$$

$$= 404.45 \text{ ms}^{-1}$$

15. ***(d)*** Kinetic energy is $\frac{3}{2}RT$ which does not depends upon the atomic mass of the gases.

16. ***(c)*** Compressibility factor is given as,

$$Z = \frac{pV}{RT} \qquad \ldots(i)$$

Given, $Z = 0.5$, $p = 100$ atm, $R = 0.0821$ L-atm/ mol-K

$T = 0°\text{C} = (0 + 273)\text{ K} = 273\text{K}$

Putting all these values in Eq. (i) we get

$$0.5 = \frac{100 \times V}{0.0821 \times 273}$$

$$V = 0.112 \text{ L}$$

Now, from van der Waals' equation $\left(p + \frac{a}{V^2}\right)(V - b) = RT$

$$\left(100 + \frac{a}{(0.112)^2}\right)(0.112 - 0) = 0.0821 \times 273$$

On solving, we get, $a = 1.253 \text{ L}^2 \text{ mol}^{-2}\text{atm}$

17. ***(b,c)*** Let p_{H_2} and p_{un} be the partial pressure of hydrogen and unknown gas, respectively and n' be the number of moles of unknown gas

Now, from ideal gas equation, $pV = nRT \Rightarrow p = \frac{n}{V}RT$

For H_2, $p_{H_2} = \frac{0.7}{3} \times 0.0821 \times 300$ $\qquad \ldots(i)$

For unknown gas, $p_{un} = \frac{n'}{3} \times 0.0821 \times 300$ $\qquad \ldots(ii)$

Adding Eq.(i) and Eq.(ii),

$$p_{H_2} + p_{un} = \frac{1}{3} \times 0.0821 \times 300(0.7 + n')$$

But total pressure, i.e. $p_{H_2} + p_{un} = 6$ (Given)

$$\therefore \qquad 6 = \frac{1}{3} \times 0.0821 \times 300(0.7 + n')$$

or $\qquad n' = 0.0308$ mol

Now, from Graham's law of effusion, $\frac{r_{H_2}}{r_{un}} = \sqrt{\frac{M_{un}}{M_{H_2}}}$

where, r_{H_2} and r_{un} are rates of effusion of H_2 and unknown gas; M_{H_2} and M_{un} are molecular masses of H_2 and unknown gas, respectively.

$$\therefore \qquad \frac{0.7}{20} / \frac{0.0308}{20} = \sqrt{\frac{M_{un}}{2}}$$

or $\qquad M_{un} = 1033 \text{ g mol}^{-1}$

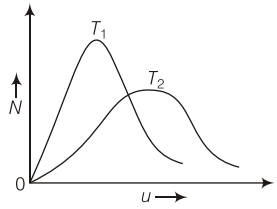
Mass of unknown gas is given as,

Mass = Number of moles $\times$ molecular mass

or Mass = $0.0308 \times 1033 = 31.81$ g

18. ***(a)***

19. ***(a,b,c)*** Distribution of molecules (N) with velocity (u) at two temperatures T_1 and T_2 $(T_2 > T_1)$ is shown below



At both temperature, distribution velocity first increases, reaches a maximum value and then decreases.

20. ***(a,b)*** $(u_{r_{ms}})_{He} = \sqrt{\frac{3RT}{4}}$ $\left(\because u_{rms} = \frac{\sqrt{3RT}}{M}\right)$

$$(u_{rms})_{SO_2} = \sqrt{\frac{3RT}{64}}$$

$$\therefore \quad \frac{(u_{rms})_{He}}{(u_{rms})_{SO_2}} = \sqrt{\frac{64}{4}} = \frac{4}{1}$$

$$\Rightarrow \quad (u_{rms})_{SO_2} = \frac{1}{2}(u_{rms})_{He} \qquad \text{(Given)}$$

$$\therefore \quad \sqrt{\frac{3RT}{64}} = \frac{1}{2}\sqrt{\frac{3R \times 300}{4}}$$

or $T = 1200$ K

$\Rightarrow$ Since, u_{rms} does not depend upon p and V, there will be no effect on speed by changing volume.

$\Rightarrow$ Since u_{rms} does not depend upon number of molecules, speed will not be changed by change in number of molecules.

21. ***(a,b,c,d)***

22. ***(a,b,c)*** At high pressure: $pV > RT$.

23. ***(a,b,d)*** If a gas is collected over water, vapour are mixed with the collected gas. Hence, the corrected pressure of the gas must be used, as given below

$$p_{gas(dry)} = p_{total(moist\ gas)} - p_{water\ vapour}$$

Percentage of a gas in a mixture is given as

$$= \frac{\text{Partial pressure of gas } (p)}{\text{Total pressure } (p)} \times 100$$

This law is applicable for gaseous components which do not react with each other. e.g. $N_2 + O_2$, $CO + CO_2$, $N_2 + Cl_2$ etc.

Relative humidity (R_H) is calculated as

$$R_H = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$

24. ***(a,c,d)*** Initially, mass of butane in the cylinder

$= (29.0 - 14.8)$ kg

$= 14.2$ kg

Pressure (p) = 2.5 atm,

Temperature (T) = 300 K and molecular mass of butane = 58 g mol^{-1}.

Using ideal gas equation,

$$pV = nRT = \frac{w}{M}RT \qquad \ldots(i)$$

where, w and M are mass and molecular mass of gas respectively.

Putting values in Eq.(i)

$$2.5 \times V = \frac{14.2 \times 10^3}{58} \times 0.0821 \times 300$$

$$V = 2.4 \times 10^3 \text{L} = 2.4 \text{ m}^3 \qquad (\because 1 \text{ m}^3 = 1000 \text{ L})$$

After the use the mass of the remaining gas

$= (23.2 - 14.8)$ kg

$= 8.4 \times 10^3$ g

The volume remains constant, now again using ideal gas equation,

$$pV = \frac{w}{M}RT$$

$$p \times 2.4 \times 10^3 = \frac{8.4 \times 10^3}{58} \times 0.0821 \times 300$$

$$\Rightarrow \quad p = 1.50 \text{ atm}$$

Therefore, decrease in pressure

$= 2.5 - 1.5 = 1.0$ atm

Mass of gas used

$= (29.0 - 23.2)$ kg

$= 5.8$ kg $= 5.8 \times 10^3$ g

Again using ideal gas equation,

$$pV = \frac{w}{M}RT$$

$$\therefore \quad 1 \times V = \frac{5.8 \times 10^3}{58} \times 0.0821 \times 300$$

$$V = 2.4 \times 10^3 \text{L} = 2.4 \text{ m}^3$$

25. ***(b)*** Let 'α' be the degree of dissociation of Cl_2.

$$Cl_2 \rightleftharpoons 2Cl$$

At equilibrium, $1 - \alpha$ 2α

Total number of moles at equilibrium

$$\Rightarrow \quad 1 - \alpha + 2\alpha = 1 + \alpha$$

From diffusion information,

$$\frac{r_{(mix)}}{r_{(Kr)}} = 1.16 = \sqrt{\frac{84}{M_{(mix)}}}$$

$$\Rightarrow \quad M_{(mix)} = 62.4$$

Now, $\frac{\text{Normal molar mass}}{\text{Experimental molar mass}} = 1 + \alpha$

or $\frac{71}{62.4} = 1 + \alpha$

or $\alpha = 0.14$, i.e. 14%

26. ***(c)*** We have the relation,

$$p(V - b) = RT$$

$$\Rightarrow \quad pV - pb = RT$$

$$\frac{pV}{RT} = \frac{pb}{RT} + 1$$

$$\Rightarrow \quad Z = \frac{pb}{RT} + 1 \qquad \left(\because Z = \frac{pV}{RT}\right)$$

where, p = Pressure

b = Real gas constant

R = Gas constant

T = Temperature

V = Volume

Z = Compressibility factor.

Hence, $Z > 1$ at all pressures, which means repulsive tendencies will be dominant when interatomic distance are small. Which also means the interatomic potential is never negative but becomes positive at small interatomic distances.

27. ***(d)*** Diffusioin coefficient (DC) $\propto \lambda$ (mean free path) $\propto U_{mean}$

Thus (DC) $\propto \lambda U_{mean}$

But, $\lambda = \frac{RT}{\sqrt{2}\, N_0 \sigma p}$

$$\lambda = \frac{T}{p}$$

and $U_{mean} = \sqrt{\frac{8RT}{\pi M}}$

$U_{mean} \propto \sqrt{T}$

$\therefore$ $DC \propto \frac{(T)^{3/2}}{p}$

$(DC)_2 = X\,(DC)_1$

or $X = \frac{(DC)_2}{(DC)_1}$

$X = \left(\frac{p_1}{p_2}\right)\left(\frac{T_2}{T_1}\right)^{3/2}$

$= \left(\frac{p_1}{2p_1}\right)\left(\frac{4T_1}{T_1}\right)^{3/2}$

$= \left(\frac{1}{2}\right)(8) = 4$

28. ***(a,b)*** $NH_3(l)$ is highly volatile liquid. When NH_3 molecules are enclosed in a bottle, they generates a high pressure inside the bottle. When the bottle is opened, there is chances of bumping of stopper. To avoid this bumping, the closed bottle of $NH_3(l)$ should be cooled due to which pressure inside the bottle gets lowered.

At Boyle temperature, the first virial coefficient (B) vanishes and real gas approaches ideal behaviour.

$$T_B = \frac{a}{Rb}$$

A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal kinetic energy.

According to Graham's law of diffusion

Rate of diffusion of gas

$$\propto \frac{1}{\sqrt{\text{Molecular weight of gas}}}$$

29. ***(c)*** Given,

$$u_{rms} = u_{mps}$$

or, $\sqrt{\frac{3RT}{M(X)}} = \sqrt{\frac{2RT}{M(Y)}}$

On squaring both sides,

$$\frac{3RT}{M(X)} = \frac{2RT}{M(Y)}$$

or $\frac{3R \times 400}{40} = \frac{2R \times 60}{M(Y)}$

$$M(Y) = 4 \text{ g mol}^{-1}$$

30. ***(d)*** According to van der Waals' equation.

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$\Rightarrow$ $a = \frac{V^2}{n^2}\left[\frac{nRT}{V - nb} - p\right]$

$= \frac{4^2}{2^2}\left[\frac{2 \times 0.082 \times 300}{4 - 2(0.05)} - 11\right]$

$= 6.46 \text{ atm L}^2\text{mol}^{-2}$.

CHEMISTRY IN action!

New Vitamin B_2-powered battery

Vitamins may be good for our health; likewise they might also be good for powering batteries. In the latest version of an organic flow battery (which uses carbon-based organic compounds instead of metal ions to carry charges) scientists have introduced a molecule similar to the core of vitamin B2 to carry energy. Like other flow batteries, this one stores energy in two liquids and generates an electrical current as the liquids flow past each other, trading electrons across a membrane. As the liquids can be housed in large tanks, these batteries presumed to have the potential to store days' worth of energy from renewable sources such as wind and sun.

Two years ago, researchers created the first organic flow battery using a compound commonly found in rhubarb. Now, the same group reports the development of same type battery from ALLOXAZINE, the back bone of vitamin B_2. If the new battery can be scaled up, it would be cheaper to produce than the metal variety, as the B_2 compound can be readily made from common starting materials at room temperature. Plus, it would be less toxic.

PERSONALITIES SPECTRUM

ROSALIND FRANKLIN
(25/07/1920-16/04/1958)

All that is necessary for faith is the belief that by doing our best we shall come nearer to sucess and that success in our aims is worth attaining.

British chemist Rosalind Franklin is best known for her role in the discovery of the structure of DNA, and for her pioneering use of X-ray diffraction.

Rosalind Franklin was extremely intelligent. She knew by the age of 15 that she wanted to be a scientist in her future. She learned crystallography and X-ray diffraction techniques that she applied to DNA fibers. One of her photographs provided key insights into DNA structure. Other scientists used it as the basis for their DNA model and took credit for the discovery.

LIFE HISTORY

British chemist Rosalind Elsie Franklin was born into a wealthy and influential Jewish family on July 25, 1920 at Notting Hill, in London, England.

She received her education at several schools including North London Collegiate School, where she excelled in science, among other things.

Rosalind Franklin enrolled at Newnham College, Cambridge, in 1938 and studied chemistry. In 1941, she was awarded Second Class Honors in her finals, then she works as an assistant research officer at the British Coal Utilisation Research Association, where she studied the porosity of coal. This work was the basis of her 1945 Ph.D. thesis "The physical chemistry of solid organic colloids with special reference to coal."

In the fall of 1946, Franklin was appointed at the Laboratoire Central des Services Chimiques de l'Etat in Paris, where she worked with crystallographer Jacques Mering. He taught her X-ray diffraction, which would largely play a role into her discovery of "the secret of life"—the structure of DNA. In addition, Franklin pioneered the use of X-rays to create images of crystalised solids in analysing complex, unorganised matter, not just single crystals.

In the fall of 1956, Franklin found that she was suffered with ovarian cancer. Inspite of this she continued working throughout the following two years, having three operations and experimental chemotherapy. She experienced a 10-month remission and worked up until several weeks before her death on April 16, 1958, at the age of 37.

CONTRIBUTION TO CHEMISTRY

Franklin was an English chemist and X-ray crystallographer who made contributions to the understanding of the molecular structures of DNA (deoxyribonucleic acid), RNA (ribonucleic acid), viruses, coal and graphite. Although her works on coal and viruses were appreciated in her lifetime, her contributions to the discovery of DNA were largely recognised after her death.

Her work on the X-ray diffraction images of DNA while at King's College, London, which led to the discovery of the DNA double helix for which James Watson, Francis Crick and Maurice Wilkins shared the Nobel Prize in Physiology or Medicine in 1962. Watson suggested that Franklin would have ideally been awarded a Nobel Prize in Chemistry, alongwith Wilkins, but the Nobel Committee does not make dead people nominations.

After finishing her work on DNA, Franklin led pioneering work at Birkbeck on the molecular structures of viruses. Her team member Aaron Klug continued her research, winning the Nobel Prize in Chemistry in 1982.

FREDERICK SANGER
(13/08/1918-19/11/2013)

Scientific research is one of the exciting and rewarding of occupations.

Frederick Sanger was a British biochemist who won the Nobel Prize for Chemistry twice, one of only two people to have done so in the same category (the other is John Bardeen in Physics) the fourth person overall with two Nobel Prizes, and the third person overall with two Nobel Prizes in the sciences.

LIFE HISTORY

Frederick Sanger was born on August 13, 1918. He was educated at Bryanston School. At St. John's College, Cambridge, where he took his B.A. degree in natural sciences in 1939. He has been carried out research in the Department of Biochemistry at Cambridge since 1940. From 1940 to 1943 he worked with Dr. A. Neuberger on the metabolism of the amino acid lysine and obtained a Ph. D degree in 1943. From 1944 to 1951 he held a Beit Memorial Fellowship for Medical Research. Then, he has been a member of the External Staff of the Medical Research Council since 1951. His last position was head of the Division of Protein Chemistry in the MRC Laboratory for Molecular Biology, at Cambridge University in Gloucestershire.

His work has been concerned largely with problems related to the determination of the structure of proteins. Since, 1943 these studies resulted in the determination of the structure of insulin

Sanger died in his sleep at Addenbrooke's Hospital in Cambridge on 19 November 2013. As noted in his obituary, he had described himself as "just a chap who messed about in a lab," and "academically not brilliant".

CONTRIBUTION TO CHEMISTRY

In 1951, Sanger was awarded the Corday-Morgan Medal and Prize of the Chemical Society. In 1954, he became a Fellow of the Royal Society and a Fellow of King's college, Cambridge. He was an Honorary Foreign Member of the American Academy of Arts and Sciences, American Society of Biological Chemists, Member of the Academies of Science of Argentina and Brazil, Japanese Biochemical Society, and Corresponding Member of the Association Quimica Argentina.

In the course of identifying the amino groups, Sanger figured out ways to order the amino acids. He was the first person to obtain a protein sequence. By doing so, Sanger proved that proteins were ordered molecules and by analogy, the genes and DNA that make these proteins should have an order or sequence as well. Sanger won his first Nobel Prize for Chemistry in 1958 for his work on the structure of protein.

Sanger initially investigated ways to sequence RNA because it was smaller. Eventually, this led to techniques that were applicable to DNA and finally to the dideoxy method most commonly used in sequencing reactions today.

Sanger won a second Nobel Prize for **Chemistry in 1980** sharing it with Walter Gilbert, for their contributions concerning the determination of base sequences in nucleic acids, and Paul Berg for his work on recombinant DNA.

CONCE
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ATOMIC ST

1 PRELIMINARY ATOMIC MODELS

(I) THOMSON'S PLUM PUDDING MODEL

This model is based on electrical neutrality. Thomson visualised atom as a pudding of positive charge which is balanced with electrons as plums embedded into it.

(II) RUTHERFORD'S ATOMIC MODEL

Rutherford bombarded highly energised positively charged helium ions on a thin film of gold foil (thickness ≈ 100 nm) surrounded by a circular fluorescent ZnS screen.

He observed that most of α-particles passed directly through the gold foil, small fraction of these deflected by small angle and very few bounced back in the reverse direction. He concluded that entire mass of the atom resides in its nucleus and is equal to the sum of protons and neutrons.

DRAWBACKS OF RUTHERFORD MODEL

- The orbital revolution of electron around the positively charged nucleus is not expected to be stable.
- It could not explain atomic spectra of H-atom and discontinuous spectrum.

2 DEVELOPMENTS LEADING TO BOHR'S MODEL OF ATOM

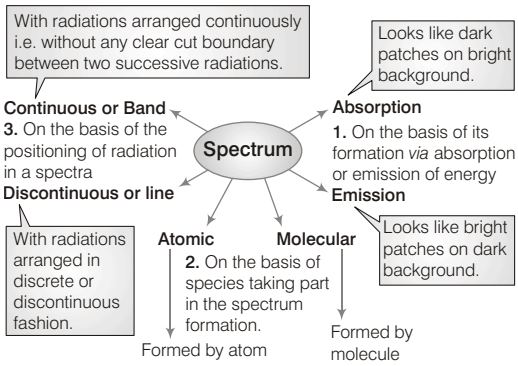
- **Dual nature of electromagnetic radiations** Electromagnetic radiations show characteristics of light wave as well as stream of light particles (photons).
- **Quantised electronic energy levels** (Planck's quantum theory) Atoms and molecules could emit or absorb energy in discrete quantities only which are called quantum. The energy of a quantum is proportional to its frequency as $E = h\nu$ and always emitted in integral multiples of $h\nu$ as $2h\nu$, $3h\nu$ etc. In other words energy is quantised.
- **Einstein explanation of quantised nature of light** Einstein suggested that light consists of stream of particles, called photons which move with the speed of light. He gave some formula related to photoelectric effect.

Property	Formula
Energy of photon, E_{photon}	$h\nu$ or $\frac{hc}{\lambda}$
Work function (W) or ionisation energy (IE)	$h\nu_0 = \frac{hc}{\lambda_0}$
Kinetic energy of photoelectron	$\frac{1}{2}mv^2 = h(\nu - \nu_0)$ $= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$

- Ionisation energy or work function is the minimum amount of energy required by an electron to escape from the metal surface.
- If $E_{photon} < W$, no photoelectron will escape.

3 SPECTRA

A spectra gives us a pictorial representation of arrangement of radiations in the increasing order of wavelength or decreasing order of frequency.


With radiations arranged continuously i.e. without any clear cut boundary between two successive radiations.
Looks like dark patches on bright background.
Continuous or Band
3. On the basis of the positioning of radiation in a spectra
Discontinuous or line
Spectrum
Absorption
1. On the basis of its formation via absorption or emission of energy
Emission
With radiations arranged in discrete or discontinuous fashion.
Atomic
Molecular
2. On the basis of species taking part in the spectrum formation.
Looks like bright patches on dark background.
Formed by atom
Formed by molecule

The ideal body, which emits and absorbs all possible frequencies is known as black body and the radiations emitted by this body are called **black body radiations.**

4 BOHR'S ATOMIC MODEL

- Electrons revolve around the nucleus in specific circular orbits having angular momentum as the integral multiple of $\frac{h}{2\pi}$, i.e. $mvr = \frac{nh}{2\pi}$, with a definite velocity. Each orbit can contain only a set of number of electrons.
- As long as electron remains in a particular orbit, it neither emits nor gains energy.
- Each stationary orbit is associated with a definite amount of energy. The greater is the distance of the orbit from the nucleus, more will be the energy associated with it.
- An electron can move from one energy level to another through quanta or photon jumps only.

Ⓐ LINE SPECTRUM OF HYDROGEN

On passing electric discharge through gaseous hydrogen molecules, these dissociate into energised hydrogen atoms which produce electromagnetic radiations of discrete frequency.

Rydberg gave the following formulae to calculate the wave number $(1/\lambda)$ associated with electromagnetic radiation emitted by different atoms of hydrogen gas molecules.

$$\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right], n_1 < n_2$$

where, $R_H = \frac{2\pi^2 m_e e^4}{ch^3}$ = Rydberg s constant

$= 109677 \text{ m}^{-1} = 10967700 \text{ cm}^{-1}$

Ⓑ LIMITATIONS OF BOHR'S MODEL

(i) It is unable to explain hydrogen atom spectrum (doublet, triplet etc.) observed by using spectroscopic techniques.

(ii) It is unable to explain the spectrum of atoms/ions having more than one electron.

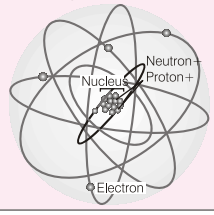
(iii) It is unable to explain the ability of atom to form molecules by chemical bonds.

5 DIFFERENT TYPES OF LINE SPECTRUM

Series of lines	n_1	n_2	Spectral region	Wavelength range
Lyman series	1	2, 3, ... ∞	UV light < 4000 Å	$1/R_H - 4/3R_H$
Balmer series	2	3, 4, ... ∞	Visible 4000 – 7000 Å	$4/R_H - 36/5R_H$
Paschen series	3	4, 5, ... ∞	Near IR > 7000 Å	$9/R_H - 144/7R_H$
Brackett series	4	5, 6, ... ∞	IR > 7000 Å	$16/R_H - 400/9R_H$
Pfund series	5	6, 7, ... ∞	Far IR > 7000 Å	$25/R_H - 900/11R_H$
Humphrey series	6	7, 8, ... ∞	Far IR > 7000 Å	$36/R_H - 1764/13R_H$

- Atom is the smallest particle of an element that retains all the chemical properties of the element.
- Atom consists of many subatomic particles, like, electrons, protons, neutrons, mesons, positrons, antiprotons, quarks, pions and gluons, etc. The properties and location of three major subatomic particles, electron, proton and neutron are given in right hand side table

Subatomic particles
Electron (e)
Proton (p)
Neutron (n)



Here, charges
Coloumb) for

6 BOHR'S FORMULAE FOR HYDR

Property	For
Bohr radius	$r_n = \frac{n^2}{4\pi^2 K}$
Bohr energy (a) Kinetic energy of an electron (KE)	KE = $\frac{2\pi^2}{}$
(b) Potential energy of an electron (PE)	PE = $\frac{-4\pi^2}{}$
(c) Total energy E = KE + PE	$E = \frac{-2\pi^2}{r}$
(d) Velocity of electron (v_n)	$v_n = \frac{2\pi KZ}{nh}$
(e) Time period of revolution of an electron (T_n)	$T_n = \frac{}{4\pi^2 r}$
(f) Orbital frequency $\left(\nu_n = \frac{1}{T_n}\right)$	$\nu_n = \frac{4\pi^2 n}{}$

7 DEVELOPMENTS LEADI MODEL OF AN ATOM

- **dE-BROGLIE EQUATION**
  According to de-Broglie, like photon,
  i.e. $\lambda = \frac{h}{p} = \frac{h}{mc} = \frac{1}{\sqrt{2m}}$
- **HEISENBERG'S UNCERTAINTY P**
  According to this, exact position and e
  be calculated precisely. Mathematical

PT MAP
ision Tool
TRUCTURE

Properties of Subatomic Particles

Charge	Mass (kg)	Mass amu	Location in the atom	Discoverer
–1	9.1×10^{-31}	0.005	Outside the nucleus	J.J. Thomson
+1	1.67×10^{-27}	1	In the nucleus	Ernest Rutherford
0	1.67×10^{-27}	1	In the nucleus	James Chadwick

are given in the multiple of electronic charge (1.602×10^{-19} convenience.

ROGEN AND HYDROGEN LIKE SPECIES

mulae	Numerical value
$\frac{h^2}{me^2Z}$	$r = 0.529\left(\frac{n^2}{Z}\right)$ Å
$\frac{nK^2Z^2e^4}{n^2h^2}$	KE $= 13.6\left(\frac{Z^2}{n^2}\right)$ eV atom^{-1}
	$= 21.8 \times 10^{-19}\left(\frac{Z^2}{n^2}\right)$ J atom^{-1}
$\frac{mK^2Z^2e^4}{n^2h^2}$	PE $= -27.2\left(\frac{Z^2}{n^2}\right)$ eV atom^{-1}
$\frac{nK^2Z^2e^4}{n^2h^2}$	$E = -13.6\left(\frac{Z^2}{n^2}\right)$ eV atom^{-1}
	$= -21.8 \times 10^{-19}\left(\frac{Z^2}{n^2}\right)$ Jatom^{-1}
$\frac{e^2}{}$	$v_n = 2.188 \times 10^6\left(\frac{Z}{n}\right)$ ms^{-1}
$\frac{n^3h^3}{nK^2Z^2e^4}$	$T_n = 1.5 \times 10^{-16}\left(\frac{n^3}{Z^2}\right)$ s
$\frac{nK^2Z^2e^4}{n^3h^3}$	$v_n = 6.66 \times 10^{15}\left(\frac{Z^2}{n^3}\right)$ s^{-1}

NG TO QUANTUM MECHANICAL

electron has both momentum and wavelength.

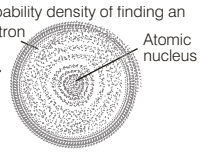
$\overline{uE}$

RINCIPLE

exact velocity or momentum of a subatomic particle cannot lly, $\Delta p \times \Delta x \geq \frac{h}{4\pi}$ or $\Delta v \times \Delta x \geq \frac{h}{4\pi m}$ or $\Delta E \times \Delta t \geq \frac{h}{4\pi}$

8 QUANTUM MECHANICAL MODEL OF AN ATOM

Quantum mechanical model of an atom deals with probability rather than exact position or velocity. To find the electron in a particular region. Schrodinger gave the following equation for defining the wave motion of an electron in 3D space.



$$\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} + \frac{8\ ^2m}{h^2}(E \quad V) \quad = 0$$

Here, x, y and z are space coordinates, m is mass of an electron h is Planck constant, E is total energy, V is potential energy of electron and is amplitude of an electron wave called wave function.

DIFFERENCE BETWEEN AND ^{2}

Variable quantity describes the wave characteristics of a particle.	It measures ^{2} probability density at a point in an atom.
It can be negative (here positive or negative sign defines direction of wave).	It can never be negative.

9 ORBITAL SUBSHELL AND ORBIT

Orbital A three dimensional region in which probability of finding an electron is maximum. An orbital can accommodate maximum of two electrons with exactly equal energy.

Subshell Aggregation or group of orbitals of exactly similar energy. Subshells are named as s, p, d and f.

Orbit An orbit is an imaginary 2D circular path around the nucleus, where probability of finding an electron is maximum. The maximum number of electrons in nth orbit, is equal to $2n^2$ (n = number of orbit).

10 DEGENERATE AND NON-DEGENERATE ORBITALS

Orbitals which have same energy are called degenerate while orbitals which do not have same energy are called non-degenerate orbitals. e.g. p_x, p_y and p_z ⊳ Degenerate orbitals s, p, d and f ⊳ Non-degenerate orbitals

11 RULES RELATED TO FILLING ELECTRONS IN ORBITALS

Aufbau principle Orbitals are filled up according to increase in their energy. The order of increasing energy level can be calculated by $(n+l)$ rule, which states that

- Lower the value of $(n+l)$ for an orbital lower is its energy.
- If two orbitals have same value of $(n+l)$, the orbital with lower value of n will be filled first. Order in which electrons are filled in orbitals is as follows $1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d<7p$

Hund's rule The pairing of electrons in the orbitals of a particular subshell (p, d or f) does not take place until all the orbitals of a subshell are singly occupied.

Pauli's exclusion principle No two electrons in an atom can be represented by same values of all quantum numbers.

12 PERIODWISE EXCEPTIONAL ELECTRONIC CONFIGURATION

PERIOD-4

1. Cr(24) - [Ar], $3d^5, 4s^1$ **2.** Cu(29) - [Ar], $3d^{10}, 4s^1$

PERIOD - 5

3. Nb(41) - [Kr], $4d^4, 5s^1$ **4.** Mo(42) - [Kr], $4d^5, 5s^1$

5. Ru(44) - [Kr], $4d^7, 5s^1$ **6.** Rh(45) - [Kr], $4d^8, 5s^1$

7. Pd(46) - [Kr], $4d^{10}, 5s^0$ **8.** Ag(47) - [Kr], $4d^{10}, 5s^1$

PERIOD - 6

9. La(57) - [Xe], $6s^2, 5d^1$

10. Ce(58) - [Xe], $6s^2, 4f^1, 5d^1$

11. Gd(64) - [Xe], $6s^2, 4f^7, 5d^1$

12. Pt(78) - [Xe], $6s^1, 4f^{14}, 5d^9$

13. Au(79) - [Xe], $6s^1, 4f^{14}, 5d^{10}$

PERIOD - 7

14. Ac(89) - [Rn], $7s^2, 6d^1, 5f^0$

15. Th(90) - [Rn], $7s^2, 6d^2, 5f^0$

16. Pa(91) - [Rn], $7s^2, 6d^1, 5f^2$

17. U(92) - [Rn], $7s^2, 5f^3, 6s^1$

18. Np(93) - [Rn], $7s^2, 5f^4, 6d^1$

19. Cm(96) - [Rn], $7s^2, 5f^7, 6d^1$

20. Lr(103) - [Rn], $7s^2, 5f^{14}, 7p^1$

The reason behind these exceptional electronic configurations is that half-filled and fully-filled subshells have got extra stability

13 QUANTUM NUMBERS

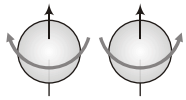
Four quantum numbers are necessary to characterise completely particular electrons in a particular orbit.

Ⓐ **Principal quantum number** (n) It defines the principal shell in which electron is revolving
Principal quantum number (n) 1, 2, 3, 4,
Letter designation K, L, M, N
Maximum number of electrons ($2n^2$) 2, 8, 18, 32.

Ⓑ **Azimuthal quantum number** (l) It describe the name of subshell and shape of orbital in which electron is present can have value 0 to (n-1).
Azimuthal quantum number (l) 0, 1, 2, 3
Subshell s, p, d, f Shape Spherical, dumbbell, double dumbbell, complicated

Ⓒ **Magnetic quantum number** (m) It describes the splitting of spectral lines under the influence of magnetic field. When $n = 1, l = 0$ and $m = 0$, there exist one spherical s-orbital. When, $n = 2, l = 1$ and $m =$ 1,0,+1, there exists three degenerate p-orbitals. When $n = 3, l = 2$ and $m =$ 2, 1,0 + 1,+2.
There exists five degenerate d-orbitals.

Ⓓ **Spin quantum number** It describes the rotation of electron either in clockwise or anti clockwise direction on its own axis. The spin quantum number is either equal to $+\frac{1}{2}$ or $\frac{1}{2}$.

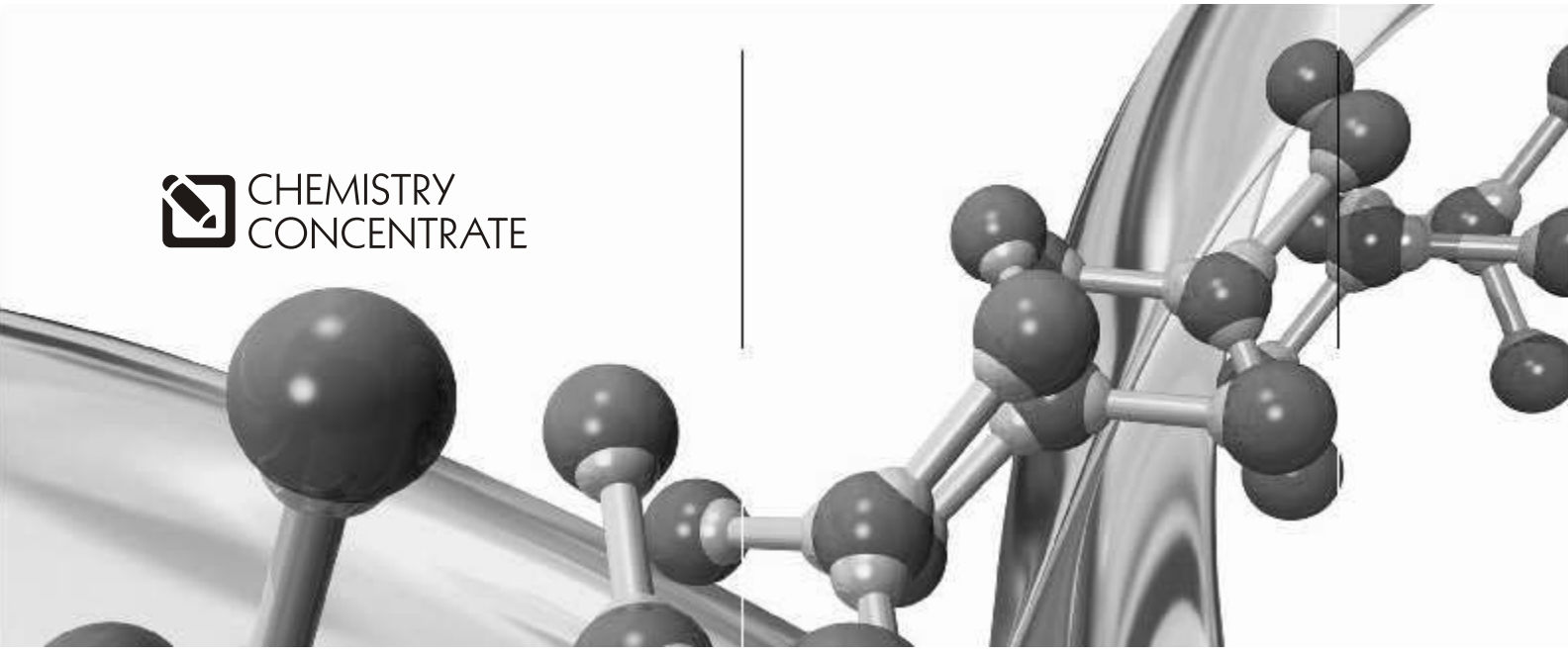


14 RADIAL NODE, ANGULAR NODE AND NODAL PLANE

- A **radial node** is the spherical region around nucleus where probability of finding an electron is zero as shown in the figure for 2s orbital. Similarly, if such a distribution is seen at an angle from the nucleus, the node is called **angular node**. For an orbital, number of nodes can be calculated as
  Number of radial nodes = n l 1
  Number of angular nodes = l
  Total nodes = n l
- The number of radial nodes signifies the energy of an orbital. Larger the number of nodes, higher will be the energy of orbital.
- Number of radial node increases with increase in principal quantum number.
- A ns-orbital has (n 1) radial nodes.
- Nodal plane represents the plane having zero probability of finding an electron.

1s orbital

2s orbital



EQUILIBRIA

A FREE ENERGY PERCEPTION

The prediction of all chemical or physical changes around us, is done by the difference between the free energies of reactants and products. The sign of free energy change tells us in which direction the reaction has to proceed in order to attain equilibrium. In this article we shall discuss how free energy plays a major role in equilibria?

Equilibrium

- A reversible reaction is one that can be made to go in either direction.This reaction takes infinite time for completion.
  e.g. for the following reversible reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If we mix carbon monoxide with water in the gas phase at a high temperature, hydrogen and carbon dioxide are produced.

Forward reaction

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

- Initially, the two compounds, $CO(g)$ and $H_2O(g)$, begin to react at a certain rate, as the reaction proceeds, the concentrations of CO and H_2O gradually decreases because both reactants are being used up. In turn, the rate of forward reaction gradually decreases.

Backward reaction

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$$

- At first, the reverse reaction is very slow. As the concentrations of H_2 and CO_2 (produced by the forward reaction) gradually increase, the rate of the backward reaction also gradually increases.
- Eventually, when the two rates become equal. At this state, we say that the process is in equilibrium and this state is known as **equilibrium state**.

Equilibrium Constant

For a general reversible reaction,

$$\underbrace{aA + bB}_{\text{Reactants}} \rightleftharpoons \underbrace{cC + dD}_{\text{Products}}$$

At equilibrium, rate of forward reaction = Rate of backward reaction.

or $$K_f[A]^a[B]^b = K_b[C]^c[D]^d \text{ or } \frac{K_f}{K_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Here, K_f and K_b are rate constants or velocity constants of forward and backward reactions, respectively.

$$\frac{K_f}{K_b} = K$$

K, is called equilibrium constant.

- Thus, at equilibrium, the ratio of concentrations of products and reactants is constant.
- For gaseous species, the ratio of partial pressures of products and reactants is constant.

Gibbs Free Energy (G)

- Gibbs free energy is an hypothetical infinite energy which drives all the spontaneous processes from higher energy state to lower energy state.
- $\Delta_r G$ is the difference in molar Gibbs energy between the products and the reactants.
- For a general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

$\Delta_r G$ = Sum of Gibbs free energies of products − Sum of Gibbs free energies of reactants.

$$\therefore \quad \Delta_r G = (c\Delta_C G + d\Delta_D G) - (a\Delta_A G + b\Delta_B G)$$

- For standard conditions,

$$\Delta_r G^\circ = (c\Delta_C G^\circ + d\Delta_D G^\circ) - (a\Delta_A G^\circ + b\Delta_B G^\circ)$$

or, in general

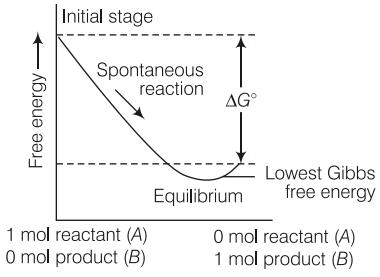
$$\Delta_r G^\circ = \Sigma v_i \Delta G^\circ_{(\text{Products})} - \Sigma v_i \Delta G^\circ_{(\text{Reactants})}$$

Where, v_i = Stoichiometric coefficient of corresponding species either reactant or product.

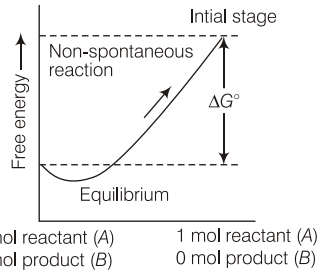
Role of Gibbs Free Energy in the Achievement of Equilibrium

Consider the following reaction, $A \longrightarrow B$

- At constant temperature and pressure, a spontaneous reaction moves from higher Gibbs energy to lower Gibbs energy. For more details consider the following figure.



- As you can see in the above figure, at any stage during the reaction, Gibbs free energy of the system is decreasing as the reaction proceeds.
- The lowest Gibbs free energy is achieved when the reactant(s) is/are completely converted into product(s).
- However, once the system reaches at lowest Gibbs free energy, it does not further proceed in the forward direction. If the reaction continues after lowest Gibbs free energy, the Gibbs energy would increase and the process would be non-spontaneous.
- Hence, the composition of the reaction mixture does not change beyond lowest Gibbs free energy, which represents the equilibrium composition of the reaction.
- Beyond equilibrium point, the reaction becomes non-spontaneous and shown by the figure given above on RHS.



- For further reaction beyond equilibrium point, we need to supply some energy in order to proceed the reaction.
- For non-spontaneous reaction ΔG° comes out to be positive, i.e. now, Gibbs free energy keeps on increasing or you can say that you have to supply a continuous increasing amount of energy in order to get back at initial stage.

REMEMBER

For homogeneous reactions, the equilibrium composition will never contain 100% products, no matter how much lower their free energy relative to the reactants is.

Example 1 Identify the correct statement for change of Gibbs energy for a system (ΔG_{System}) at constant temperature and pressure. **[IIT 2008]**

(a) If $\Delta G_{\text{System}} > 0$, the process is spontaneous
(b) If $\Delta G_{\text{System}} = 0$, the system has attained equilibrium
(c) If $\Delta G_{\text{System}} = 0$, the system is still moving in a particular direction
(d) If $\Delta G_{\text{System}} < 0$, the process is not spontaneous

Sol. **(b)** At constant temperature and pressure, if Gibbs free energy for a system (ΔG_{System}) is equal to zero, then system will present in a state of equilibrium.

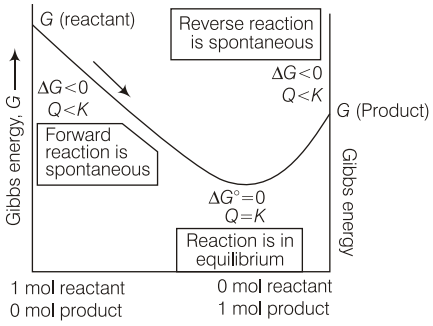
Prediction of Direction for a Reaction by Gibbs Free Energy

- If a reaction is not at equilibrium, the amount of products and reactants change until they reach the equilibrium composition.
- Since, the proportions of reactant(s) and product(s) change, as the reaction proceeds, therefore, Gibbs energy of the system also changes.
- To investigate change in G, a measure of the composition of the reaction mixture is needed (as reaction mixture changes during the reaction).
- To measure the composition of the reaction mixture at any given time we use a term named as "Reaction Quotient (Q)"

$$Q = \frac{\Pi(a_{\text{products}})}{\Pi(a_{\text{reactants}})} \qquad \ldots(\text{i})$$

- Here, (a_{Products}) and ($a_{\text{Reactants}}$) are activities of products and reactants, respectively.
- Π means multiplication of all the species alongwith this sign.
- For reactions which take place in the gaseous phase, use partial pressure terms in place of activities.
- For reactions which take place in liquid phase, use concentration terms in place of activities.

- The reaction quotient provides an additional way to predict the direction of reaction. This is summarised in the figure given below.



i.e. when $\Delta G < 0, Q < K \Rightarrow$ Forward reaction is spontaneous

When $\Delta G = 0, Q = K \Rightarrow$ Reaction is in equilibrium

When $\Delta G > 0, Q > K \Rightarrow$ Reverse reaction is spontaneous or forward reaction is non-spontaneous.

Example 2 Consider the following reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At 510°C, $K = 46$, if hydrogen gas, iodine vapour and hydrogen iodide, each at a partial pressure of 0.55 bar, are mixed, predict the direction of the reaction.

(a) Forward (b) Backward
(c) At equilibrium (d) Can't predict

Sol. **(a)** For gaseous species,

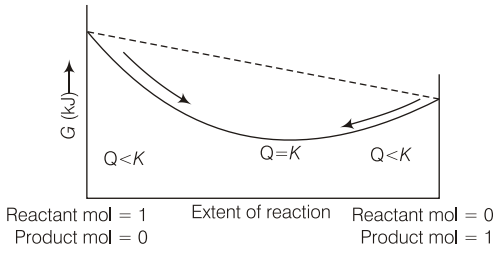
$$\text{Reaction quotient } (Q) = \frac{p^2_{HI}}{p_{H_2} \times p_{I_2}} = \frac{(0.55)^2}{(0.55) \times (0.55)} = 1$$

The direction of the reaction is decided by the value of Q.

As, $Q < K$, the forward reaction takes place, so more HI will form.

Relation between Gibbs Free Energy and Equilibrium Constant

- A reaction reaches equilibrium when it reaches its minimum Gibbs energy at constant temperature and pressure. The concentrations of reactant(s) and product(s) are related by equilibrium constant. Thus, there must be a quantitative relationship between equilibrium constant and Gibbs free energy. For more understanding consider the figure given above on RHS.



- At the far left, the graph drops faster than the straight line from $G_{\text{Reactants}}$ to G_{Products}. The slope at any point on the curve differs from the slope of straight line ($\Delta G°$) by a factor that depends on the reaction quotient Q.

$$\text{Slope} = \Delta_r G° + RT \ln Q \quad \ldots(i)$$

or $$\text{Slope} = \Delta_r G = \Delta_r G° + 2.303 RT \log Q \quad \ldots(ii)$$

At equilibrium, Slope = 0, $Q = K$

Thus, eq (i) reduces to $\Delta_r G° = -RT \ln K \quad \ldots(iii)$

For expression of K, eq (iii) can be rearranged as :

$$K = e^{-\left(\frac{\Delta_r G°}{RT}\right)} = \text{Antilog}\left(-\frac{\Delta_r G°}{2.303\ RT}\right)$$

Where, K = Equilibrium constant,
$\Delta_r G$ = Standard Gibbs energy change
R = Gas constant
T = Temperature
e = Exponential

GIBBS FREE ENERGY AND EQUILIBRIUM CONSTANT

Different types of problems can be asked in the exam from either of calculation of Gibbs free energy or equilibrium constant.

Type 1 When temperature and equilibrium constant are given and standard Gibbs energy change is asked to find, use the following formula.

$$\Delta G° = -RT \log K = -2.303\ RT \log K \quad \ldots(i)$$

Type 2 When $\Delta_r G°$ and temperature (T) are given and equilibrium constant is asked to find out, use the following formula

$$K = e^{-(\Delta_r G°/RT)} = \text{Antilog}\left(\frac{-\Delta_r G°}{2.303\ RT}\right) \quad \ldots(ii)$$

Type 3 When temperature (T), equilibrium concentrations of reactants and products are given, $\Delta G°$ is asked to find out, use the following steps.

Step I Find out equilibrium constant value with the help of given equilibrium concentration values $K = \frac{\Pi[\text{Products}]}{\Pi[\text{Reactants}]}$

Step II Put the value of K in eq (i) (mentioned in Type 1)

Type 4 When Gibbs energy changes for reactants and products are given, equilibrium constant is asked to find out, use the following steps.

Step I Calculate $\Delta_r G°$ as,

$$\Delta_r G° = \sum v_i \Delta G°_{(\text{Products})} - \sum v_i \Delta G°_{(\text{Reactants})}$$

Step II Put the value of $\Delta_r G°$ in eq(ii) (mentioned in Type 2)

Example 3 Consider the following equilibrium at 25°C,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

If equilibrium constant (K) is 1.8×10^{-7}, find the value of $\Delta G°$ (in kJ mol^{-1})

(a) 48.38 (b) 49.27
(c) 38.48 (d) 34.24

Sol. **(c)** We know that,

$$\Delta G° = -2.303\, RT \log K_C \quad \ldots(i)$$

Given,

$T = (25 + 273)\,K = 298\,K$,
$K_C = 1.8 \times 10^{-7}$,
$R = 8.314\ J\ K^{-1} mol^{-1}$

Putting all these values in eq (i), we get

$$\Delta G° = -2.303 \times 8.314 \times 298 \log (1.8 \times 10^{-7})$$
$$= 38484\ J\ mol^{-1}$$
$$= 38.484\ kJ\ mol^{-1}$$

Example 4 For the water gas reaction,

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

the standard Gibbs free energy of reaction at 1000 K is -8.1 kJ mol^{-1}. Calculate its equilibrium constant.

(a) 1.00 (b) 2.65 (c) 1.78 (d) 3.79

Sol. **(b)** As we know that,

$$K = e^{-(\Delta G°/RT)} = \text{Antilog}\left(-\frac{\Delta G°}{2.303\, RT}\right) \quad \ldots(i)$$

Given, $\Delta G° = -8.1\ kJ\ mol^{-1}$, $R = 8.314 \times 10^{-3}\ kJ\ K^{-1} mol^{-1}$, $T = 1000\ K$

Putting these value in eq (i), we get

$$K = \text{Anti log}\left(\frac{-(-8.1)}{2.303 \times 8.314 \times 10^{-3} \times 1000}\right)$$

$K = 2.65$

Example 5 The equilibrium concentrations of the species in the reaction, $A + B \rightleftharpoons C + D$ are 3, 5, 10 and 15 mol L^{-1} respectively. At 300 K, the ΔG (in cal) for the reaction is

(a) 13.81 (b) -1381.8
(c) -138.18 (d) 1391.6

Sol. **(c)**

	A	+ B	$\rightleftharpoons$	C	+ D
At equilibrium	3	5		10	15

$$\text{Equilibrium constant} = \frac{[C][D]}{[A][B]}$$
$$= \frac{10 \times 15}{3 \times 5} = 10$$

$\because \quad \Delta G = -2.303\, RT \log K$

$\therefore \quad \Delta G = -2.303 \times 2 \times 300 \log 10 \quad [R = 2\ cal\ mol^{-1} K]$
$= -2.303 \times 2 \times 300 \times 1$
$= -1381.8\ cal$

Example 6 Methanol is synthesised by the use of following reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Calculate the equilibrium constant for the reaction at 298 K.
($\Delta_f G°_{298}$ (kJ mol^{-1}); $CO(g) = -137.2$; $H_2(g) = 0$; $CH_3OH(g) = -162.0$)

(a) 1.1×10^{-4} (b) 1.1×10^{4}
(c) 2.2×10^{-4} (d) 2.2×10^{4}

Sol. **(d)** $\Delta_r G°_{298} = \sum v_i \Delta_f G°_{298}(\text{Products}) - \sum v_i \Delta_f G°_{298}(\text{Reactants})$

$= [\Delta_f G°_{298}(CH_3OH(g))] - [\Delta_f G°_{298}(CO(g)) + 2 \times \Delta_f G°_{298}(H_2(g))]$

$= -162.0 - (-137.2 + 0)$
$= -24.8\ kJ\ mol^{-1}$

Now, from $\Delta_r G° = -2.303\, RT \log K$

or $-24.8 \times 10^3 = -2.303 \times 8.314 \times 298 \times \log K$

or $$\log K = \frac{24.8 \times 10^3}{2.303 \times 8.314 \times 298}$$

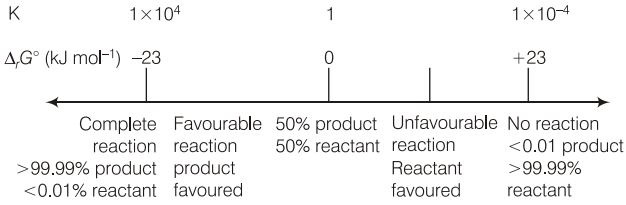
$= 4.35$

or $K = \text{Antilog}\ (4.35)$

$K = 2.2 \times 10^4$

Prediction of Equilibrium Composition with Gibbs Free Energy Change

- The Gibbs free energy change, not only tells us whether a reaction is spontaneous or non-spontaneous but also gives an indication of the equilibrium composition of the reaction.



Thus, we may lead to the following conclusions from above figure.

- If $\Delta_r G°$ is negative, K must be greater than 1. Similarly, if $\Delta_r G°$ is positive, K must be less than 1.
- A more negative value of $\Delta_r G°$ gives a large value of K and greater proportion of products at equilibrium.
- Similarly, a more positive value of $\Delta_r G°$ gives a small value of K and a greater proportion of reactant at equilibrium.
- A reaction with more negative value of $\Delta_r G°$ than -22.8 kJ mol^{-1} will effectively go to completion.
- A reaction with more positive value of $\Delta_r G°$ than $+22.8$ kJ mol^{-1} will not occur noticeble extent. Only 0.01% extent of products obtain.

Feasibility of a Chemical Reaction

We can summarised feasibility of a reaction in the table given below.

Gibbs energy change $\Delta_r G°$ (kJ mol^{-1})	Equilibrium constant (K)	Feasibility of reaction
<0	>1	Feasible
>0	<1	Non-feasible
Equals to zero	Equals to 1	At equilibrium

Example 7 Calculate the Gibbs energy change at 750 K for a reaction $R \rightleftharpoons P$, that produces 99.99% product at equilibrium?

(a) – 57.4 kJ mol^{-1} *(b)* 57.4 kJ mol^{-1}
(c) 60.92 kJ mol^{-1} *(d)* – 60.92 kJ mol^{-1}

Sol. ***(a)*** Equilibrium constant K can be calculated as :

$$K = \frac{[P]}{[R]} = \frac{99.99\%}{(100 - 99.99)\%} = \frac{99.99\%}{0.01\%} = 9999$$

Now, $\Delta_r G° = -RT \ln K = -(8.314 \text{ JK}^{-1}\text{mol}^{-1}) \times 750 \text{ K} \times \ln(9999)$

$= -57400 \text{ J mol}^{-1} = -57.4 \text{ kJ mol}^{-1}$

Smart Practice

1. The equilibrium constant at 25°C for the following process

$Co^{3+}(aq) + 6NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{3+}(aq)$ is 2×10^7. Calculate the value of $\Delta G°$ (in kJ mol^{-1}) at 25°C. ($R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$)

(a) – 41.658 *(b)* –10.341 *(c)* – 9.078 *(d)* – 11.092

Hint $\Delta G° = -2.303\, RT \log K$

2. For the following reaction,

$HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq)$ at 25°C, Gibbs energy change is 21.3 kJ mol^{-1}. Find out the value of equilibrium constant.

(a) 1.8×10^4 *(b)* 1.8×10^{-4} *(c)* 1.1×10^3 *(d)* 1.1×10^{-3}

Hint $K = e^{-\Delta G°/RT} = \text{Antilog}\left(-\frac{\Delta G°}{2.303\, RT}\right)$

3. The free energy change $\Delta G = 0$, when

(a) the reactants are completely consumed
(b) a catalyst is added
(c) the system is at equilibrium
(d) the reactants are intially mixed

Hint When, $\Delta G = 0$, equilibrium constant $K = 1$, i.e. system is at equilibrium.

4. Consider the following isomerisation reaction

$$n\text{-butane}(g) \rightleftharpoons \text{Isobutane}(g)$$

Given, ΔG_f° (n-butane) = – 15.9 kJ mol^{-1}

and ΔG_f° (iso-butane) = – 18 kJ mol^{-1} at 298 K.

Determine the mole percentage of isobutane, in the given thermodynamic conditions.

(a) 30% *(b)* 70% *(c)* 40% *(d)* 60%

Hint $\Delta_r G° = \Delta G°$ (iso-butane) $- \Delta G°$ (n-butane)

Now, $\Delta_r G° = -RT \ln K$

n-butane $(g) \rightleftharpoons$ iso-butane (g)

Initial moles	1	0
At equilibrium	$1 - x$	x

$$K = \frac{x}{1 - x}$$

5. Heating cupric oxide (CuO) at 400°C does not produce any appreciable amount of Cu.

$$CuO(s) \rightleftharpoons Cu(s) + \frac{1}{2}O_2;\ \Delta G° = 127.2 \text{ kJmol}^{-1}$$

However, if this reaction is coupled to the conversion of graphite to carbon monoxide, it becomes spontaneous. Determine the equilibrium constant for the coupled reaction.

(Given ΔG_f° of CO $(g) = -137.3$ kJmol^{-1})

(a) 2.3 *(b)* 1.2 *(c)* 6.1 *(d)* 8.9

Hint $CuO(s) \rightleftharpoons Cu(s) + \frac{1}{2}O_2,\ \Delta G° = 127.2 \text{ kJmol}^{-1}$ ...(i)

$C(s) + \frac{1}{2}O_2(g) \rightleftharpoons CO(g);\ \Delta G° = 137.3 \text{ kJmol}^{-1}$ ...(ii)

On coupling Eq (i) and (ii), we get

$CuO(s) + C(s) \rightleftharpoons Cu(s) + CO(g)$

6. The standard reaction free energy change for the ionisation of a weak monobasic acid in water is 32 kJmol^{-1}. What is the percentage of the molecules of acid ionised in a 0.10 M aqueous solution of acid?

(a) 0.496% *(b)* 0.982% *(c)* 0.329% *(d)* 0.410%

Hint $K_a = \text{Antilog}\left(\frac{-\Delta G°}{2.303\, RT}\right)$

$HA \rightleftharpoons H^+ + A^-$

$K_a = C\alpha^2$

7. The pressure of saturated vapour over solid benzene at 268.2 K is 2279.8 Pa and that of a saturated vapour over supercooled benzene (l) is 2639.7 Pa. Calculate the change in Gibbs free energy in the course of solidification of 1 mole of supercooled benzene at the above temperature.

(a) – 327 J *(b)* 500 J *(c)* 327 J *(d)* – 500 J

Hint $C_6H_6(l) \rightleftharpoons C_6H_6(s)$

$\Delta G° = -nRT \ln K$

$K = \frac{p_{C_6H_6(s)}}{p_{C_6H_6(l)}}$

8. 1-pentyne (A) on heating at 175°C in presence of concentrated KOH, produces an equilibrium mixture of 1.3% (A), 95.2% 2-pentyne (B) and 3.5% 1, 2-pentadiene (C). Calculate free energies for

$$B \longrightarrow A, \Delta G_1^\circ;\ B \longrightarrow C, \Delta G_2^\circ$$ [IIT 2007]

(a) 17.79 kJ mol^{-1} and 12.30 kJ mol^{-1}
(b) 12.30 kJ mol^{-1} and 15.99 kJ mol^{-1}
(c) 16.00 kJ mol^{-1} and 10.30 kJ mol^{-1}
(d) 12.30 kJ mol^{-1} and 10.30 kJ mol^{-1}

Hint For $B \rightleftharpoons A$, $K_1 = \frac{1.3}{95.2} = 13.6 \times 10^{-3}$

$\Rightarrow \quad \Delta G_1^\circ = -RT \ln K_1$

For $B \rightleftharpoons C$, $K_2 = \frac{1.3}{95.2} = 36.76 \times 10^{3}$

$\Rightarrow \quad \Delta G_2^\circ = -RT \ln K_2$

9. The equilibrium constant for the reaction, $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ at 298 K is 73. Calculate the value of the standard free energy change. ($R = 8.314$ JK^{-1} mol^{-1})

(a) 12.922 kJ mol^{-1} *(b)* – 12.922 kJ mol^{-1}
(c) 10.632 kJ mol^{-1} *(d)* – 10.632 kJ mol^{-1}

Hint $\Delta G^\circ = -2.303\, RT \log K$

10. Calculate ΔG° for the conversion of oxygen to ozone, $\frac{3}{2} O_2(g) \rightleftharpoons O_3(g)$ at 298 K, if K_p for this conversion is 2.47×10^{-29}

(a) 163.228 kJ mol^{-1} *(b)* – 163.228 kJ mol^{-1}
(c) 163.228 J mol^{-1} *(d)* – 163.228 J mol^{-1}

Hint $\Delta G^\circ = -2.303\, RT \log K_p$

11. For the ammonia synthesis reaction at 25°C, calculate the change in Gibbs free energy if 1 mol $N_2(g)$ at 0.23 bar and 3 mol of $H_2(g)$ at 0.42 bar are converted to 2 mol $NH_3(g)$ at 1.45 bar

$$\Delta G_f^\circ\ (NH_3 = -16.45 \text{ kJ mol}^{-1})$$

(a) 18.79 kJ mol^{-1} *(b)* – 18.79 kJ mol^{-1}
(c) 20.96 kJ mol^{-1} *(d)* – 20.96 kJ mol^{-1}

Hint $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\Delta G^\circ = 2(\Delta G_f^\circ (NH_3(g)) - \{(\Delta G_f^\circ (N_2(g) + 3(\Delta G_f^\circ (H_2(g))\}$$

$$Q = \frac{p_{NH_3}^2}{p_{N_2} p_{H_2}^3}$$

$\therefore \quad \Delta G = \Delta G^\circ + RT \ln Q$

12. In the following equilibrium,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given, $\Delta G_{f(N_2O_4)}^\circ = 100$ kJ and $\Delta G_{f(NO_2)}^\circ = 50$ kJ

Find ΔG of the reaction at 298 K and direction of reaction. [IIT 2009]

(a) – 5.705 kJ, forward *(b)* – 5.705 kJ, backward
(c) 2.497 kJ, backward *(d)* – 2.497 kJ, forward

Hint Reaction quotient $(Q_p) = \frac{[p_{NO_2}]}{p_{N_2O_2}} = \frac{100}{10} = 10$

$$\Delta G^\circ_{reaction} = 2\Delta G^\circ_{f(NO_2)} - \Delta G^\circ_{(N_2O_4)}$$

We know that, $\Delta G = \Delta G^\circ - 2.303\, RT \log Q_p$

13. Consider the following reaction at equilibrium

$$K + L \rightleftharpoons M + N$$

Find the equilibrium concentration ratio $[M]$ to $[K]$ ($\Delta G^\circ = 460$ Cal)

(a) 0.439 *(b)* 0.682
(c) 0.721 *(d)* 0.989

14. The value of $\log_{10} K_p$ for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 25°C would be if the standard enthalpy of formation of $NH_3(g)$ is – 40 kJ and standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 191, 130, 192 JK^{-1}mol^{-1}, respectively.

(a) 5.0 *(b)* 5.845
(c) 2.7585 *(d)* None of these

Hint $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

15. K_p for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 400°C is 1.64×10^{-4}. What will be the value of ΔG° if equilibrium constant is equal to K_p?

(a) + 11.733 kcal *(b)* – 11.733 kcal
(c) + 1.0733 kcal *(d)* – 1.0733 kcal

16. The partial pressure of reactants H_2, CO_2, H_2O and CO are 10, 20, 0.02 and 0.01 atm respectively. $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

Given, ΔG_f° for $H_2(g)$, $CO_2(g)$, $H_2O(g)$ and $CO(g)$ are 0, –394.37, –228.58, – 137.15 kJ, respectively. Choose the correct option regarding the direction of reaction.

(a) Forward
(b) Backward
(c) Neither backward nor forward
(d) Cannot predict

17. Ice and water are in equilibrium at 273 K, which of the following option is correct?

(a) $\Delta_r G_{ice} > \Delta_r G_{H_2O}$ *(b)* $\Delta_r G_{ice} < \Delta_r G_{H_2O}$
(c) $\Delta_r G_{ice} = \Delta_r G_{H_2O}$ *(d)* $\Delta_r G_{ice} = \Delta_r G_{H_2O} \neq 0$

18. Which of the following options will be correct for the stage of half completion of the reaction, $A \rightleftharpoons B$?

(a) $\Delta G^\circ = 0$
(b) $\Delta G^\circ > 0$
(c) $\Delta G^\circ < 0$
(d) $\Delta G^\circ = -RT \log 2$

Hint $\Delta G^\circ = -RT \ln K$

At the stage of half completion of reaction $[A] = [B]$. Therefore, $K = 1$, thus $\Delta G^\circ = 0$.

19. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the standard free energy change is greater than zero. The equilibrium constant (K) would be
(a) $K = 0$ (b) $K > 1$
(c) $K = 1$ (d) $K < 1$

20. For the reaction at 298 K
$A(g) + B(g) \rightleftharpoons C(g) + D(g)$
$\Delta H° = -29.8$ kcal, $\Delta S° = -0.100$ kcalK^{-1}.
The value of $\Delta G°$ will be
(a) 0 (b) 1
(c) 1.07 (d) 2

21. Inversion of cane sugar is based on the following hydrolysis:
$C_{12}H_{12}O_{11} + H_2O \rightleftharpoons C_6H_{12}O_6 + C_6H_{12}O_6$
K_C is found to be 2×10^{14} at 400 K. The value of $\Delta G°$ at 400 K would be
(a) – 109.53 kJ mol^{-1}
(b) 109.53 kJ mol^{-1}
(c) Neither (a) nor (b)
(d) 123.0 kJ mol^{-1}

22. Phosphorylation of glucose is non-spontaneous reaction and at 300 K, $\Delta G°$ is found to be 14.0 kJ mol^{-1}. What would be the value of thermodynamic equilibrium constant K_C?
(a) 3.654×10^{-3} (b) 3.654
(c) 5.0×10^{-4} (d) 6.2×10^{-4}

23. For the equilibrium,
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$
The $\Delta H°$ and $\Delta S°$ at 300K and 1200K for the forward reaction are as follows:
$\Delta H°_{300\,K} = 41.16$ kJ mol^{-1}
$\Delta S°_{300\,K} = -0.0424$ kJ mol^{-1}
$\Delta H°_{1200\,K} = -32.93$ kJ mol^{-1}
$\Delta S°_{1200\,K} = -0.0296$ kJ mol^{-1}
In which direction will the reaction be spontaneous at 300 K?
(a) Forward
(b) Reverse
(c) At equilibrium
(d) Data is insufficient

24. If the equilibrium constant for a reaction is very small (say 1×10^{-20}), what would the value of ΔG expected to be?
(a) A small positive number (b) A large positive number
(c) A small negative number (d) A large negative number

25. If the $E°_{cell}$ for a given reaction has a negative value, which gives the correct relationship for the values of $\Delta G°$ and K_{eq}?
(a) $\Delta G° > 0; K_{eq} < 1$ (b) $\Delta G° > 0; K_{eq} > 1$
(c) $\Delta G° < 0; K_{eq} > 1$ (d) $\Delta G° < 0; K_{eq} < 1$

26. If $\Delta G°$ at 25°C for the reaction,
$\frac{1}{2}N_2(g) + \frac{3}{2} \rightleftharpoons NH_3(g)$ is -16.5 kJ mol^{-1} then thermodynamic equilibrium constant is equal to?
(a) 1.08 (b) 7.80×10^2
(c) 4.57×10^6 (d) 7.98×10^{34}

27. Enthalpy and entropy change for a chemical reaction are -2.5×10^3 cal and 7.4 cal deg^{-1} respectively. At 25°C, the reaction is
(a) reversible (b) irreversible
(c) spontaneous (d) non-spontaneous

28. The equilibrium constant (K_C) for the following reaction at 298 K is
$$3\,Sn^{4+} + 2Cr \longrightarrow 3Sn^{2+} + 2Cr^{3+}.$$
[Given $E°_{cell} = 0.887$V; $n = 6$]
(a) 1×10^{90} (b) 1×10^{19}
(c) 1×10^{20} (d) 1×10^{39}

29. At 300 K,
$A \rightleftharpoons$ Product ; $\Delta G°_T = -200$ kJ mol^{-1}
$B \rightleftharpoons$ Product ; $\Delta G°_T = -100$ kJ mol^{-1}.
Thus, ratio of equilibrium constant at 300 K is
(a) 2 (b) 100 (c) 0.5 (d) 0.01

30. Minimum temperature at which following reaction will be spontaneous is
$$A \rightleftharpoons B \; ; \; \Delta H = 50 \text{ kcal mol}^{-1}$$
$$\Delta S = 100 \text{ cal K}^{-1}$$
(a) 490 K (b) 500 K
(c) 501 K (d) 500.1 K
Hint $\Delta G = \Delta H - T\Delta S$

Answers

1. (a)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (c)	**6.** (a)	**7.** (a)	**8.** (a)	**9.** (d)	**10.** (a)
11. (d)	**12.** (a)	**13.** (b)	**14.** (b)	**15.** (a)	**16.** (a)	**17.** (d)	**18.** (a)	**19.** (d)	**20.** (a)
21. (b)	**22.** (a)	**23.** (a)	**24.** (b)	**25.** (a)	**26.** (b)	**27.** (c)	**28.** (a)	**29.** (b)	**30.** (d)

AMAZING REALITIES

German chemist Alfred Von Baeyer was the first person to invent synthetic indigo dye. In fact, he even won a Nobel Prize for this in 1905.

50 BEST QUESTIONS ON ALCOHOLS, PHENOLS & ETHERS FOR MEDICAL ENTRANCES

1. Consider the following reaction.

$$B \text{ (Mix)} \xleftarrow{\text{Aqueous HI}} (CH_3)_3C{-}OCH_3 \xrightarrow{\text{Anhydrous HI}} A \text{ (Mix)}$$

Which of the following statements is correct regarding the above reaction?

(a) *A* and *B* are identical mixtures of CH_3I and $(CH_3)_3$ COH

(b) *A* and *B* are identical mixtures of $(CH_3)_3CCl$ and CH_3OH

(c) *A* is a mixture of CH_3I and $(CH_3)_3COH$ while *B* is a mixture of CH_3OH and $(CH_3)_3CCl$

(d) *A* is a mixture of CH_3OH and $(CH_3)_3CCl$ while *B* is a mixture of CH_3I and $(CH_3)_3COH$

2. The conversion of *m*-nitrophenol to resorcinol involves three steps, respectively

(a) hydrolysis, diazotisation and reduction

(b) diazotisation, reduction and hydrolysis

(c) hydrolysis, reduction and diazotisation

(d) reduction, diazotisation and hydrolysis

3. For the following reaction, select the statement that best describes the situation.

$$RCH_2OH + PCC \longrightarrow$$

$$(PCC = C_5H_5\overset{+}{N}HClCrO_3^-)$$

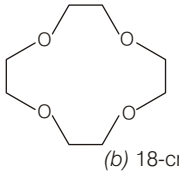
(a) The alcohol is oxidised to an acid and the Cr(VI) is reduced to Cr (III)

(b) The alcohol is oxidised to an aldehyde, and the Cr(VI) is reduced to Cr (III)

(c) The alcohol is reduced to an aldehyde, and the Cr(III) is oxidised to Cr(VI)

(d) The alcohol is oxidised to a ketone, and the Cr(VI) is reduced to Cr(III)

4. The following polyether is known as



(a) 12-crown-4 *(b)* 18-crown-6

(c) 4-crown-8 *(d)* 8-crown-4

5. Consider the following statements.

I. In the Victor-Meyer's test, the colour given by 1°, 2° and 3° alcohols are red, blue and colourless, respectively.

II. Ethyl alcohol is also called grain alcohol.

III. Phenol forms azo-dyes with benzenediazonium chloride in acidic medium.

Select the correct statement(s) and mark the correct option.

(a) Only I *(b)* I and III *(c)* I and II *(d)* II and III

6. Hydroboration-oxidation, oxymercuration-demercuration and acid catalysed hydration will give same product in

(a) *(b)* *(c)* *(d)*

7. Consider the following statements.

I. Ethers dissolve in concentrated acids to form their corresponding oxonium salts.

II. Ethers react with lewis acid to form etherates.

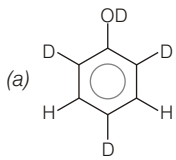
III. The cleavage of ethers by HI forms the basis of Zeisel's method.

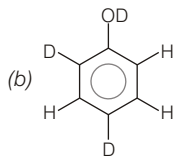
Select the correct statement(s) and mark the correct option.

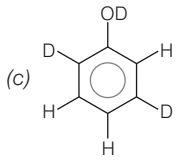
(a) Only I *(b)* I and II

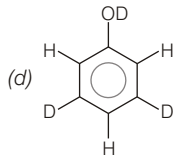
(c) III and IV *(d)* All statements are correct

8. When phenol is treated with D_2SO_4 / D_2O, some of the hydrogen gets exchanged. The final product in this exchange reaction is

(a) 

(b) 

(c) 

(d) 

9. Consider the following statements.

I. The dipole moment of alcohols is lower than that of phenols.

II. Nitrous acid reacts with 1° aliphatic amine to give 1° alcohol.

III. Lower alcohols are highly soluble in water.

IV. The reaction of phenol with benzoyl chloride in presence of NaOH is called Schotten-Baumann reaction.

Select the correct statement(s) and mark the correct option.

(a) Only I *(b)* I and II
(c) II, III and IV *(d)* All are correct

10. Among the following sets of reactants which one produces anisole?

(a) CH_3CHO, *R*Mg*X*
(b) C_6H_5OH, NaOH, CH_3I
(c) C_6H_5OH, neutral $FeCl_3$
(d) $C_6H_5—CH_3$, CH_3COCl, $AlCl_3$

11. Consider the following statements.

I. Alkyl aryl ethers are less reactive than phenols towards electrophilic substitution reactions.

II. Presence of peroxides in an old sample of ether is detected by shaking it with a freshly prepared solution of $FeSO_4$ followed by addition of KCNS.

III. In the presence of air and light, ethers form hydroperoxides.

Select the correct statement(s) and mark the correct option.

(a) Only I *(b)* II and III
(c) Only III *(d)* All are correct

12. The alcohol that produce turbidity with Lucas reagent at room temperature is

(a) 1-hydroxybutane
(b) 2-hydroxybutane
(c) 2-hydroxy-2-methylpropane
(d) 1-hydroxy-2-methylpropane

13. Consider the following statements.

I. Change in colour of acidic solution of potassium dichromate by breath is used to test drunk drivers.

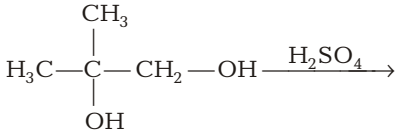
II. Methanol and ethanol are miscible in water due to covalent character.

III. Halogenation of ethers with Cl_2 or Br_2 occurs in the dark giving α-halo and α, α′-dihalo ethers.

Select the correct statement(s) and mark the correct option.

(a) Only I *(b)* II and III
(c) I and III *(d)* All are correct

14. The major product of the following reaction is



(a) $(CH_3)_2C = CH_2$
(b) butan-2-one
(c) $(CH_3)_2—CH—CHO$ (OH)
(d) iso-butyraldehyde

15. Consider the following statements.

I. Glycerol, on oxidation with conc. HNO_3 gives glyceric acid.

II. Glycerol, on oxidation with dil. HNO_3 gives a mixture of glyceric and tartonic acid.

III. Glycerol, on reaction with oxalic acid at 110°C gives allyl alcohol.

IV. Glycerol, on heating with potassium hydrogen sulphate forms alkene.

Select the correct statement(s) and mark the correct option.

(a) Only I
(b) I and II
(c) III and IV
(d) II and III

16. Which one of the following statement(s) is/are correct about phenol?

(a) Phenol turns blue litmus red
(b) It gives violet colouration with neutral $FeCl_3$
(c) It produces white ppt. with bromine water
(d) All the above statements are correct

17. Consider the following statements.

I. Phenol condenses with phthalic anhydride in the presence of conc. H_2SO_4 to form phenolphthalein.

II. Dimethyl ethers may be prepared by treating alcohols with diazomethane in the presence of HBF_4.

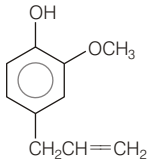
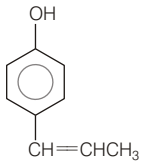
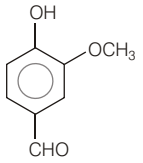
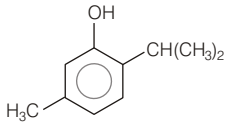
III. Salol is used as an internal antiseptic.

IV. Molasses is converted to ethanol by fermentation. The sequence of enzymes used are zymase, invertase and diastase.

Select the correct statement(s) and mark the correct option.

(a) Only I
(b) II and III
(c) III and IV
(d) I, II and III

18. Match the items given in Column I with the items given in Column II and mark the correct option from the code given below.

Column I (Phenol/Ether)	Column II (Structure)
A. Anethole	p. 
B. Eugenal	q. 
C. Tymol	r. 
D. Vanillin	s. 

Codes

	A	B	C	D		A	B	C	D
(a)	q	p	s	r	*(b)*	r	q	p	s
(c)	p	r	q	s	*(d)*	s	q	r	p

19. Consider the following statements.

I. A simple method to remove peroxides from ethers is to treat them with an aqueous solution of Br_2.

II. Williamson's synthesis of preparing dimethyl ether is free radical substitution.

III. *t*-butylmethyl ether is not prepared by the reaction of *t*-butyl bromide with sodium methoxide.

Select the correct statement(s) and mark the correct option.

(a) Only I *(b)* Only III
(c) I and II *(d)* All are correct

20. An organic compound, C_3H_6O does not give a precipitate with 2, 4-dinitrophenyl hydrazine reagent and does not react with metallic sodium. It could be

(a) CH_3–CH_2–CHO *(b)* CH_2 = CH–CH_2OH
(c) CH_3–CO–CH_3 *(d)* CH_2=CH–O–CH_3

21. Consider the following statements.

I. Phenol is soluble in *aq.*NaOH and does not evolve CO_2 with *aq.*$NaHCO_3$.

II. Secondary alcohols are easily oxidised to ketones, which are further oxidised to acids with the same number of C-atoms.

III. Glycerol is an alcohol which can be classified as monohydric alcohol.

IV. Boiling point of alcohol is comparatively higher than that of corresponding alkane due to intermolecular hydrogen bonding.

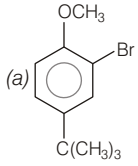
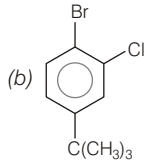
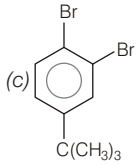
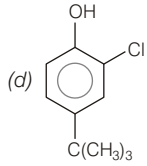
Select the correct statement(s) and mark the correct option.

(a) Only I *(b)* I and II
(c) I, II and III *(d)* All are correct

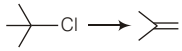
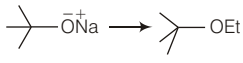
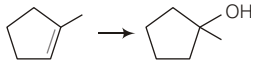
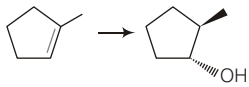
22. Consider the following reaction.

$$\text{Anisole} \xrightarrow[\text{Anhy. } AlCl_3]{(CH_3)_3CCl} A \xrightarrow{Cl_2/FeCl_3} B \xrightarrow[\Delta]{HBr} C$$

The product *C* in the above series of reaction is

(a) 
(b) 
(c) 
(d) 

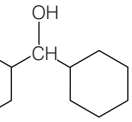
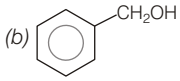
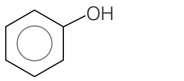
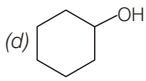
23. Match the chemical conversion in Column I with the appropriate reagent in Column II and select the correct option using the code given below the columns.

Column I	Column II
A. 	p. (i) $Hg(OAl)_2$; (ii) $NaBH_4$
B. 	q. NaOEt
C. 	r. EtBr
D. 	s. (i) BH_3; (ii) H_2O_2 / NaOH

Codes

	A	B	C	D		A	B	C	D
(a)	q	r	p	s	*(b)*	s	p	q	r
(c)	p	r	q	s	*(d)*	s	r	p	q

24. Which one of the following compounds has the most acidic nature?

(a) 
(b) 
(c) 
(d) 

25. Consider the following reaction.

$$\text{Ethanol} \xrightarrow{PBr_3} X \xrightarrow{\text{Alc. KOH}} Y \xrightarrow[\text{(ii) } H_2O,\ \text{heat}]{\text{(i) } H_2SO_4,\ \text{room temp}} Z$$

The product Z is,

(a) $CH_2=CH_2$ (b) $CH_3CH_2-O-SO_3H$
(c) $CH_3CH_2-O-CH_2CH_3$ (d) CH_3CH_2OH

26. Consider the following statements.

I. Conversion of ethyl alcohol into acetaldehyde is an example of hydrolysis.
II. Glycol can be used as an antifreeze in an automobile radiator.
III. The correct order of dehydration of alcohols is $1^\circ > 2^\circ > 3^\circ$.
IV. Denatured alcohol is a mixture of ethanol and methanol.

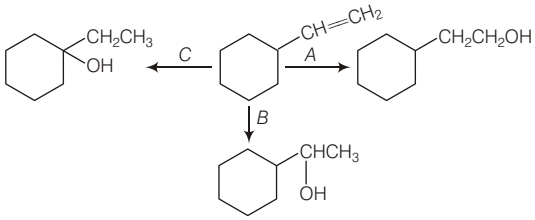
Select the correct statement(s) and mark the correct option.

(a) Only II (b) I and III (c) II and IV (d) All are correct

27. Select the ether among the following that yields methanol as one of the products on reaction with cold hydroiodic acid.

(a) 1-methoxybutane
(b) 1-methoxy-2-methylpropane
(c) 2-methoxy-2-methylpropane
(d) Methoxybenzene

28. Consider the following reactions.



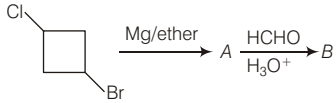
Select the schemes *A*, *B* and *C* out of

I. acid catalysed hydration.
II. hydroboration-oxidation.
III. oxymercuration-demercuration.

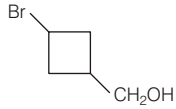
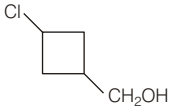
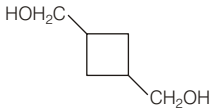
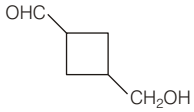
And select the correct option.

(a) I in all case (b) I, II and III (c) II, III and I (d) III, I and II

29. Consider the following reaction sequence.



The final product formed *B* is

(a) 
(b) 
(c) 
(d) 

30. Consider the following statements.

I. Glycol is used to prepare polyesters.
II. Oxo-process is also called carbonylation or hydroformylation reaction.
III. The oil of winter green is ethyl salicylate.
IV. Phenol reacts with NH_3 in the presence of anhydride $ZnCl_2$ to give aniline.

Select the correct statement(s) and mark the correct option.

(a) Only I (b) II and III
(c) I, II and IV (d) All are correct

31. Consider oxidation of following alcohols.

I. $CH_2=CHCH_2OH \xrightarrow{A} CH_2=CHCHO$

II. $(CH_3)_3COH \xrightarrow{B} CH_3-\underset{\displaystyle CH_3}{\overset{}{C}}=CH_2$

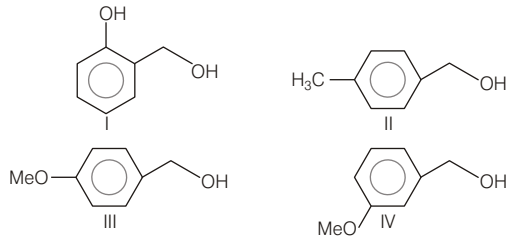
III. $CH_3CH_2OH \xrightarrow{C} CH_3COOH$

IV. $CH_3CH=CHCH_3 \xrightarrow{D} CH_3COOH$

A, *B*, *C* and *D* are oxidising agents which are respectively.

	A	*B*	*C*	*D*
(a)	MnO_2	Cu/Δ	H_2CrO_4	$KMnO_4/\Delta$
(b)	Cu/Δ	MnO_2	H_2CrO_4	$KMnO_4/\Delta$
(c)	MnO_2	Cu/Δ	$KMnO_4/\Delta$	H_2CrO_4
(d)	MnO_2	H_2CrO_4	Cu/Δ	$KMnO_4$

32. Give the decreasing order of reactivity of the following compounds with HBr.



(a) III > IV > II > I (b) III > II > IV > I
(c) II > III > IV > I (d) III > II > I > IV

33. Power alcohol is

(a) rectified spirit : benzene = 80:20
(b) rectified spirit : benzene = 20:80
(c) absolute alcohol : petrol = 80 : 20
(d) absolute alcohol : petrol = 20 : 80

34. Which one of the following reactions is possible?

(a) $Me_3C-ONa + Me_3C-Br \rightarrow Me_3C-O-CMe_3$
(b) $Me_2CH-ONa + Me_2CHBr \rightarrow Me_2CH-O-CHMe_2$
(c) $PhONa + PhBr \rightarrow PhOPh$
(d) $PhONa + CH_3Br \rightarrow PhOCH_3$

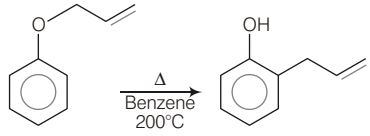
35. Which one of the following statements is wrong about the following reaction?

$$PhOEt \xrightarrow[(ii)\ H_2O]{(i)\ BBr_3} Products$$

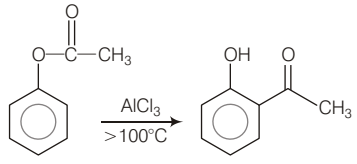
(a) BBr_3 plays a role similar as the H in HI by forming a complex with the ether $\left(Ph_2\overset{+}{O}BBr_2\right)Br^-$
(b) The liberated Br^- attacks at Et, displacing $PhOBBr_2$, which is ultimately hydrolysed to give the products
(c) The products are $PhOH + EtBr + H_3BO_3$
(d) The products are $PhBr + EtOH + H_3BO_3$

36. Match the following Column I with Column II and mark the correct option from the codes given below.

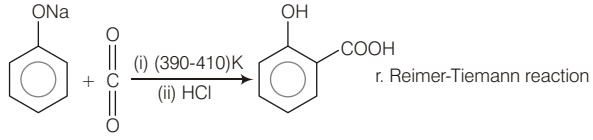
Column I (Reaction) | **Column II** (Name of reaction)

A. 

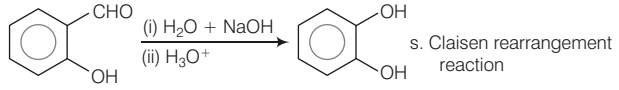
p. Dakin reaction

B. 

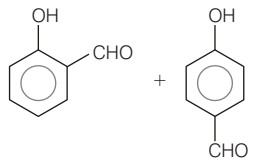
q. Kolbe-Schmitt reaction

C 

r. Reimer-Tiemann reaction

D. 

s. Claisen rearrangement reaction

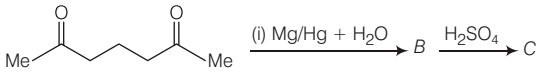
E. Phenol + $CHCl_3$ + *aq.* NaOH $\xrightarrow{340\ K}$ 

t. Fries rearrangement reaction

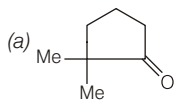
Codes

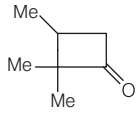
	A	B	C	D	E
(a)	q	p	r	s	t
(b)	s	t	q	p	r
(c)	t	s	p	q	r
(d)	p	q	r	s	t

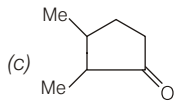
37. Consider the following reaction sequence.

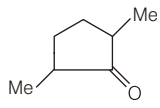


The final product formed in the above reaction is

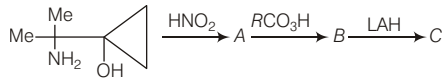
(a) 

(b) 

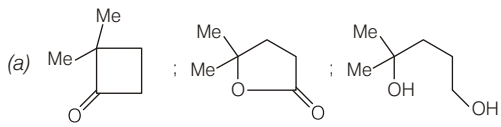
(c) 

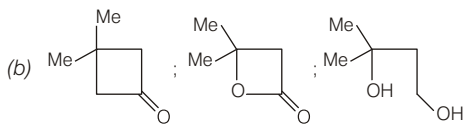
(d) 

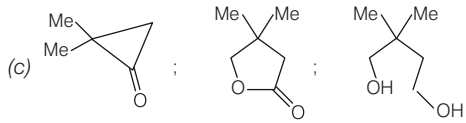
38. Consider the following reaction sequence.

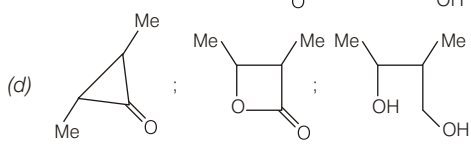


The products formed in above reaction *A*, *B* and *C*, respectively are

(a) 

(b) 

(c) 

(d) 

39. An organic compound *X* is oxidised by using acidified $K_2Cr_2O_7$. The product obtained reacts with phenyl hydrazine but does not gives silver mirror test. The possible structure of *X* is

(a) CH_3CH_2OH
(b) $(CH_3)_2CHOH$
(c) CH_3COCH_3
(d) CH_3CHO

40. Consider the following statements.

I. CF_3OH is more acidic than CH_3OH.

II. Alcohol can be protonated by a strong halogen acid to form an oxonium ion.

III. Oxymercuration-demercuration of alkene gives alcohol by rearrangement.

Choose the correct statement(s) and mark the correct option.

(a) Only I *(b)* I and II
(c) I and III *(d)* I, II and III

41. Match the items given in the Column I with items given in Column II and mark the correct option from the codes given below.

Column I	Column II
A. CH_3OH	p. Gives ketone on reaction with Cu
B. CH_3CH_2OH	q. Gives white ppt. with Lucas reagent immediately
C. $(CH_3)_2CHOH$	r. Cannot be synthesised using Grignard reagent
D. $(CH_3)_3COH$	s. Gives iodoform test

Codes

	A	B	C	D		A	B	C	D
(a)	r	s	p	q	*(b)*	r	p	q	s
(c)	q	r	p	s	*(d)*	s	r	q	p

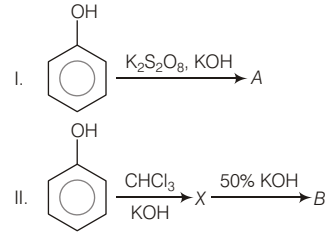
42. Arrange the following compounds in increasing order of boiling point.

Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

I II III IV

(a) I < III< II< IV *(b)* I<II< III<IV
(c) IV<II<III<I *(d)* IV< III< II< I

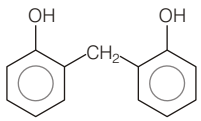
43. Consider the following reactions.



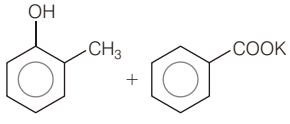
The final product formed in above reactions are

A *B*

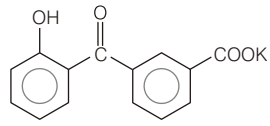
(a) Benzene-1,2-diol



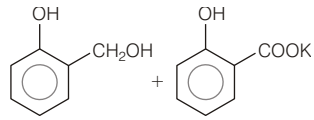
(b) Benzene-1,4-diol



(c) Benzene-1,2-diol



(d) Benzene-1, 2-diol + benzene-1,4-diol



44. Consider the following reaction sequence.

$$\text{Phenol} \xrightarrow{\text{Zn dust}} X \xrightarrow[\text{Anhy}\cdot AlCl_3]{CH_3Cl} Y \xrightarrow{\text{Alk}\cdot KMnO_4} Z$$

The product Z is

(a) benzene *(b)* benzaldehyde
(c) toluene *(d)* benzoic acid

45. Consider the following reactions.

I. $CH_3-CH(CH_3)-CH(OH)-CH_3 \xrightarrow{H^+/\text{Heat}}$

A (Major product) + *B* (Minor product)

II. $A \xrightarrow[\text{In absence of peroxide}]{\text{HBr, dark}} C + D$ (*C*: Major product; *D*: Minor product)

The major product *(A)* and *(C)*, respectively are

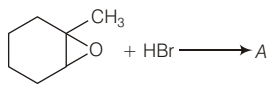
(a) $CH_2=C(CH_3)-CH_2CH_3$ and $CH_3-C(Br)(CH_3)-CH_2CH_3$

(b) $CH_2=C(CH_3)-CH_2CH_3$ and $CH_2(Br)-CH(CH_3)-CH_2CH_3$

(c) $CH_3-C(CH_3)=CH-CH_3$ and $CH_3-C(Br)(CH_3)-CH_2CH_3$

(d) $CH_3-C(CH_3)=CH_2$ and $CH_3-CH(CH_3)-CH(Br)-CH_3$

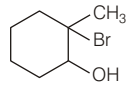
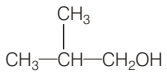
46. Consider the following reactions.

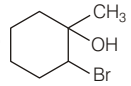
I. 

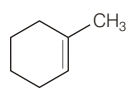
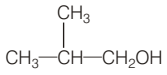
II. $CH_3-CH(CH_3)-CH_2-O-CH_2-CH_3 + HI \xrightarrow{\text{Heated}} B$

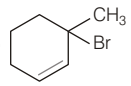
Alcohols formed in the above reaction respectively are

A B

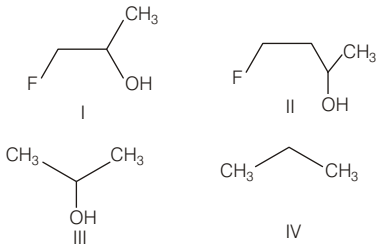
(a)  ; 

(b)  ; $CH_3—CH_2OH$

(c)  ; 

(d)  ; CH_3CH_2OH

47. The order of reactivity of the following alcohols.



towards conc HCl is

(a) IV > III > I > II (b) I > III > II > IV

(c) I > II > III > IV (d) IV > III > II > I

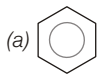
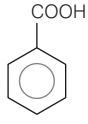
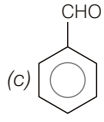
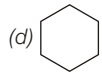
48. Match the following Column I with Column II and mark the correct option from the codes given below.

	Column I (Compound)	Column II (Order of acidity)
A.	*m*-nitrophenol, *p*-nitrophenol, *o*-nitrophenol	p. II > I > III
B.	Phenol, methyl phenol, *p*-nitrophenol	q. II > III > I
C.	Aceticacid, 2. 4, 6-trinitrophenol, phenol	r. III > I > II

Codes

	A	B	C		A	B	C
(a)	p	r	q	(b)	q	r	p
(c)	r	q	p	(d)	p	q	r

49. An organic compound *A* on treatment with $CHCl_3$ and KOH gives two compound *B* and *C*. Both *B* and *C* give the same product *D* when distilled with zinc dust. Oxidation of *D* gives *E* having molecular formula $C_7H_6O_2$. The sodium salt of *E* on heating with soda-lime gives *F* which may also be obtained by distilling *A* with zinc dust. Identify the final product formed, i.e. *E*.

(a)  (b)  (c)  (d) 

50. Which alcohol of molecular formula C_4H_9OH cannot be obtained by the reduction of carbonyl compound?

(a) 2-methylpropan-1-ol (b) 2-methylpropan-2-ol

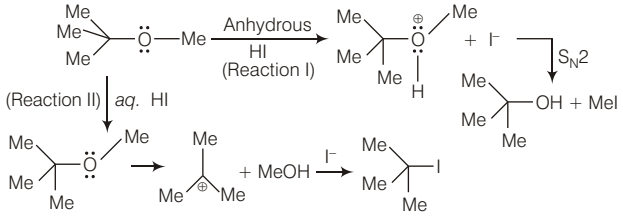
(c) Butanol (d) Butan-2-ol

Answers with Explanation

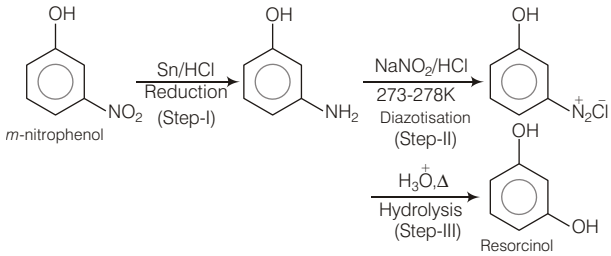
1. ***(c)*** **Thinking process**

- *The low polarity of solvent (ether) in reaction (I) favours S_N2 mechanism and the nucleophile I^- attacks at the primary carbon of (Me) group.*
- *The high polarity of solvent (¾ H_2O) in reaction (II) favours an S_N1 mechanism giving the 3°-carbocation and the nucleophile I^--attacks at the 3° carbocation of (Me_3C ¾) group.*

t-butyl methyl ether with aqueous or conc.HI, proceeds *via* S_N1 mechanism while with anhydrous HI/ether, *via* S_N2 mechanism, e.g.



2. ***(d)***

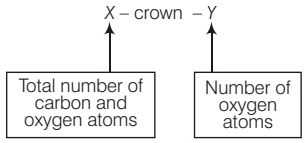


3. ***(b)*** $RCH_2OH + Cr(VI) \xrightarrow[\text{(In PCC)}]{} RCHO + Cr(III)$

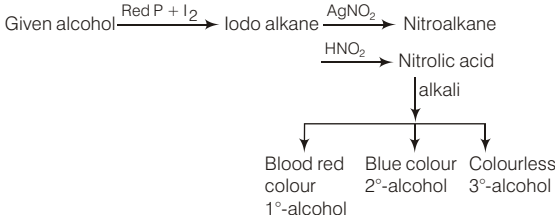
On oxidation, 1° alcohols first give aldehydes and then carboxylic acids both with same number of C-atoms as the original alcohols have. Oxidation can, however be stopped at the aldehyde stage by using either Corey's reagent, i.e.

Pyridinium chlorochromate (PCC, $C_5H_5\overset{+}{N}HClCrO_3^-$) or pyridinium dichromate (PDC, $(C_5H_5NH)_2^{2+}Cr_2O_7^{2-}$) in CH_2Cl_2 as the oxidising agent.

4. ***(a)*** 12-crown-4



5. ***(c)*** (I) **Victor-Meyer's Test** This test is used to distinguish whether a given alcohol is 1°, 2° or 3° . for the determination of this a series of reactions are involved :



6. ***(c)*** The alkene given in option (c) is a symmetric alkene,

$\therefore$ It gives same product with all the three methods.

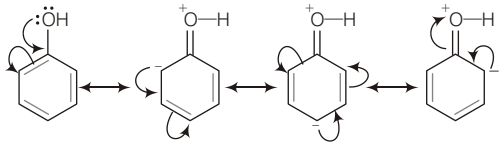
7. ***(d)***

I. Ethers act as Lewis bases and hence, dissolve in concentrated acids to form their corresponding oxonium salts.

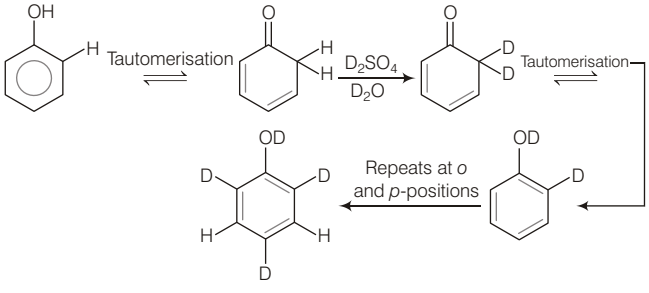
II. Being Lewis bases, ethers react with Lewis acids such as BF_3, $AlCl_3$, $FeCl_3$, Grignard reagents, etc. to form coordinate complexes called etherates.

III. Zeisel's method is used for detection of alkoxy group (methoxy, ethoxy) in an organic compound.

8. ***(a)*** **Thinking process** *In acidic medium, phenol exists in the following resonating structures.*

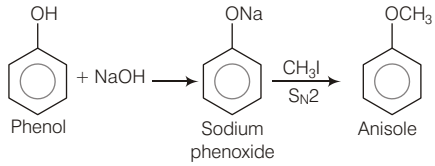


As ortho, para-positions are electron rich sites, so electrophile will attack on these sites, i.e. hydrogen of these sites get exchanged by D(deuterium).



9. ***(c)*** The C—O bond in phenols is less polar due to electron withdrawing effect of the benzene ring while in alcohols C—O bond is more polar due to + *I*-effect of the alkyl group. Therefore, dipole moment of phenols is lower than that of alcohols.

10. ***(b)***



11. ***(d)*** All the given statements are correct.

I. *I*-effect of alkoxy group (OR) > –*I*-effect of hydroxy group (—OH). Thus, alkyl aryl ethers have less electron density at *ortho* and *para*-positions than that of phenols which results in their less reactivity than phenols towards electrophilic substitution reaction.

II. Old Sample of ether + freshly prepared solution of $FeSO_4$.

Shaking
Adding KCNS
Blood red colouration

This blood red colouration confirms presence of peroxide.

III. In the presence of air and light, ethers form hydroperoxides which decompose violently on heating and causes accidents.

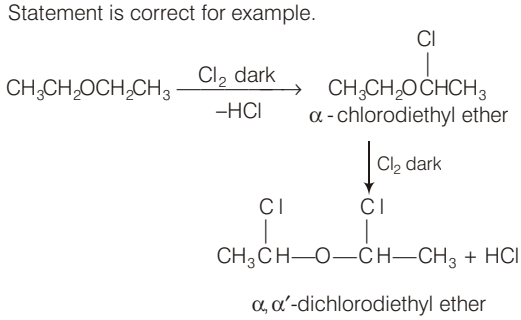
12. ***(c)*** Tertiary alcohol gives turbidity immediately with Lucas reagent. 2-hydroxy-2-methyl propane is a tertiary alcohol.

13. ***(c)***

I. Change in colour is due to the complexation of alcohol with potassium dichromate.

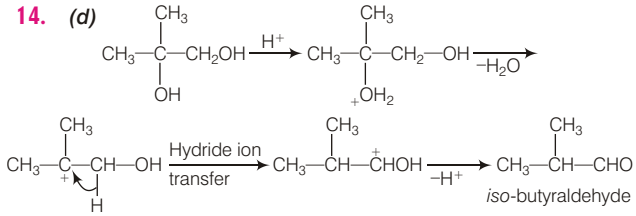
II. Methanol and ethanol are miscible in water because they show hydrogen bonding with water molecules.

III. Statement is correct for example.



However, in the presence of light and excess of chlorine, all the hydrogen atoms are substituted to give perchlorodiethyl ether.

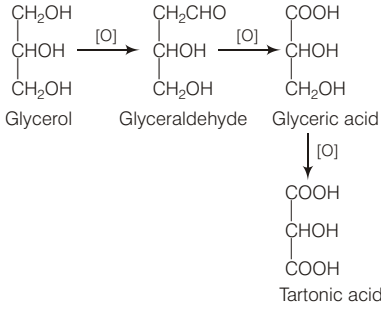
14. ***(d)***



15. ***(b)*** **Thinking process**

- *When oxalic acid is heated with glycerol at 110°C, it forms glycerol mono-oxalate which loses a molecule of CO_2 to give glycerol monoformate which in turn on hydrolysis gives formic acid.*
- *At 230°C, oxalic acid reacts with glycerol to form glycerol dioxalate which loses two molecules of CO_2 to give allyl alcohol.*

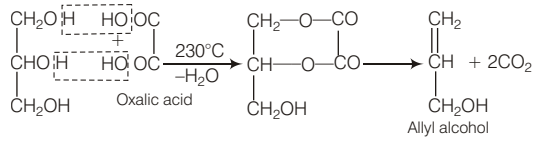
I, II- Different oxidising agents give different oxidation products on reaction with glycerol:

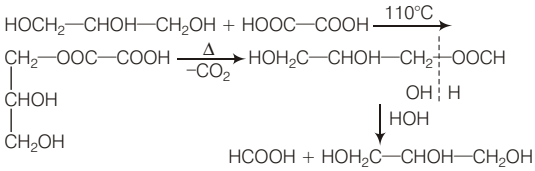


Concentrated HNO_3, oxidises glycerol mainly into glyceric acid.

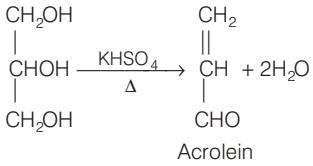
Dilute HNO_3, oxidises glycerol into glyceric acid and tartonic acid

III. At 230°C, glycerol with oxalic acid, gives allyl alcohol.





IV. Glycerol, on heating with $KHSO_4$ gives Acrolein.



16. ***(d)*** All given statements about phenol are correct.

17. ***(d)*** **Fermentation of Molasses**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

18. ***(a)*** A-q, B-p, C-s, D-r

19. ***(b)*** I. $R—X \xrightarrow{RONa} R—O—R$

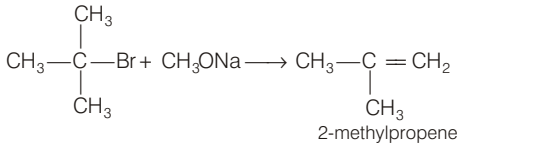
Represents a Williamson's synthesis. It involves nucleophilic substitution of the halide ion by alkoxide ion to form the alkyl halide *via* S_N2 mechanism.

II. Ether peroxide oxidises KI into I_2 and itself gets reduced to ether. Therefore, KI is added to remove peroxide from ether.

$$2I^- \longrightarrow I_2 + 2e^-$$

$$\text{ether peroxide} + 2e^- \longrightarrow \text{Ether} + O_2$$

III. As methoxide on is a strong base hence 3°-alkyl halide undergoes elimination reaction instead of nucleophilic substitution reaction.



20. ***(d)*** **Thinking process**

- *Since, the compound does not give a precipitate with 2, 4-dinitrophenyl hydrazine therefore, it cannot be an aldehyde or a ketone.*
- *Further, since it does not react with metallic sodium, therefore, it cannot be an alcohol.*

The compound C_3H_6O must be an ether,

i.e. $CH_2 = CH—OCH_3$.

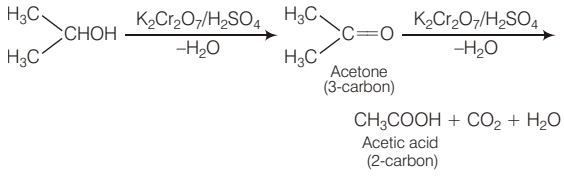
21. ***(c)***

I. Phenol is a weak acid. It reacts with NaOH to produce salt.

$$C_6H_5OH + NaOH \longrightarrow \underset{\text{Sodium phenoxide}}{C_6H_5ONa} + H_2O$$

But it is not sufficiently acidic to evolve CO_2 from $NaHCO_3$.

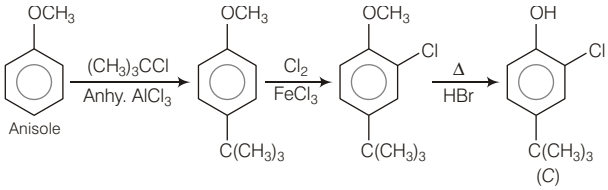
II. Secondary alcohols are easily oxidised to ketone with same number of carbon atoms, but ketone further, oxidised to carboxylic acid containing lesser number of carbon atoms than the original alcohol.



III. Glycerol is trihydric alcohol. It is $CH_2OH—CHOH—CH_2OH$. It contains three hydroxyl groups.

IV. Because of intermolecular hydrogen bonding in alcohols, they exist as associated molecules consequently, a large amount of energy is required to break these bonds and, therefore their boiling points are higher than that of the corresponding hydrocarbons.

22. ***(d)***



23. ***(a)*** A-q, B-r, C-p, D-s

C-p - Markownikoff addition of H_2O

D-s - Anti-Markownikoff addition of H_2O

24. ***(c)*** Phenoxide ion is more resonance stabilised, therefore phenol is more acidic in nature.

25. ***(d)*** $3CH_3CH_2OH \xrightarrow[-H_3PO_3]{PBr_3} 3CH_3CH_2Br \xrightarrow[-3HBr]{Alc.KOH}$

Ethanol, (X)

$$3CH_2{=}CH_2 \xrightarrow[(ii)\ H_2O,\ heat]{(i)\ H_2SO_4,\ room\ temp} 3CH_3CH_2OH$$

(Y), Ethanol (Z)

26. ***(a)***

I. Ethyl alcohol is oxidised to produce acetaldehyde

$$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO + H_2O$$

Thus, the above conversion is an example of oxidation.

II. Glycol has very low volatility as compared to other automobile radiators (methanol and water). Thus, it can be used as an automobile radiator.

III. Dehydration of alcohols involves the formation of carbocation intermediates. More the stability of carbocation, more will be the ease of dehydration of alcohols. The order of stability of carbocation is 3°>2°>1°. Therefore, the order of ease of dehydration of alcohols is 3°>2°>1°.

IV. Denatured alcohol is rectified spirit + methanol + naphthol.

27. ***(c)*** **Thinking process**

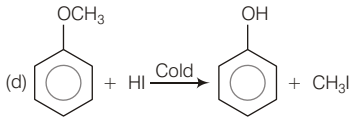
- *According to Zeisel method when an ether reacts with cold HI, alkyl iodide and alcohol are formed.*
- *In case of asymmetrical ether, the alkyl halide is always formed from the smaller alkyl group provided no tertiary (3°) alkyl group is present and if any 3° alkyl group is present, the halogen gas attached with it.*
- *In case of alkyl aryl ethers, the products are always phenol and an alkyl halide.*

(a) $CH_3{-}O{-}C_4H_9 + HI \xrightarrow{Cold} CH_3I + C_4H_9OH$

(b) $CH_3{-}O{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}CH_3 + HI \xrightarrow{Cold}$

$$CH_3I + CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}CH_2{-}OH$$

(c) $CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle OCH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_3 + HI \xrightarrow{Cold} CH_3OH + CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}I$



28. ***(c)***

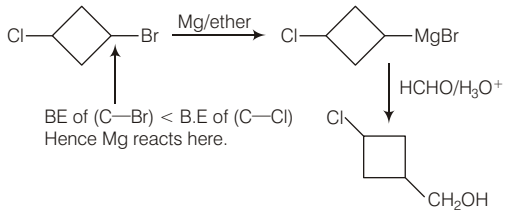
I. Hydration by Markownikoff's rule with rearrangement.

II. Hydration by anti-Markownikoff's rule.

III. Hydration by Markownikoff's rule.

Thus, *A, B, C* = II, III, I.

29. ***(b)***



30. ***(c)***

III. Methyl salicylate is the oil of winter green.

31. ***(d)***

32. ***(d)*** **Short Trick** *Electron donating group favours while electron withdrawing group retards* S_N1 *reactivity with HBr.*

Electron donating effect of (—OMe) group (+ *R*, – *I*) is greater than (– Me) group (+ *I*-effect). So, reactivity of III > II.

In (IV), (– OMe) group at *m*-position exerts only–*I*-effect and so reactivity of (IV) is less than that of (I)

So, reactivity order is III > II > I > IV.

33. ***(d)*** Power alcohol is, absolute alcohol : Petrol = 20 : 80

34. ***(d)*** **Short Trick** *Six types of ethers cannot be prepared by Williamson's synthesis.*

	RX *(Nature of carbon attached to halogen atom))*	***R*ONa** *(Nature of carbon attached to oxygen atom)*
(i)	*2°*	*2°*
(ii)	*2°*	*3°*
	3°	*2°*
(iii)	*3°*	*3°*
(iv)	*Aromatic*	*Aromatic*
(v)	*Vinyl*	*Vinyl*
(vi)	*Neopentyl*	*Neopentyl*

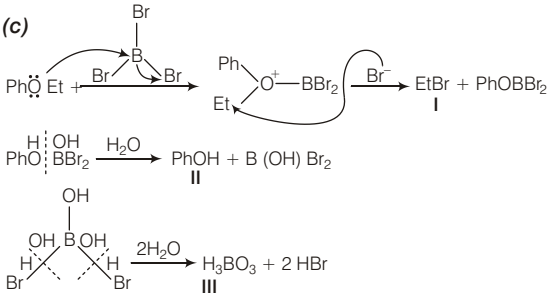
(a) Not feasible, *RX* = 3°, $R\bar{O}\overset{+}{N}a$ = 3°

(b) Not feasible, *RX* = 2°, $R\bar{O}\overset{+}{N}a$ = 2°

(c) Not feasible between Ar*X* and $Ar\bar{O}\overset{+}{N}a$

(d) Feasible, *RX* = 1° and $Ar\bar{O}\overset{+}{N}a$

35. ***(c)***

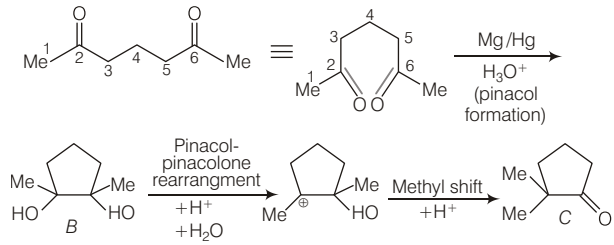


Hence, products are I, II and III, i.e. EtBr, PhOH and H_3BO_3, respectively.

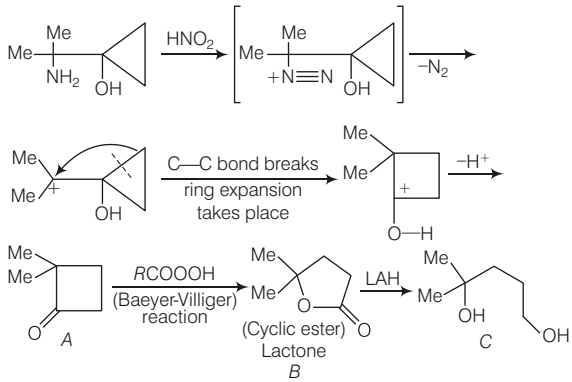
36. ***(b)*** **Fries rearrangement reaction.**

Phenolic esters with $AlCl_3$ gives *o*-and *p*-acyl phenol. At a low temperature (<100°C), *para* form predominates and at a high temperature (> 100°C), *ortho* form predominates.

37. ***(a)***

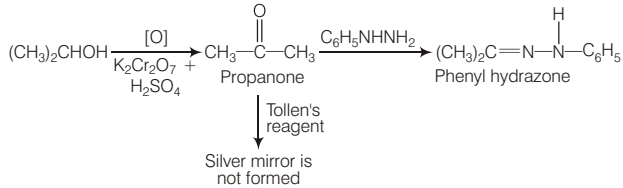


38. ***(a)***



39. ***(b)*** **Thinking process**

- *The oxidation product of X reacts with phenyl hydrazine, thus, it must contain* C ═ O *group.*
- *The same product does not give silver mirror test, thus it is a ketone because only aldehydes give this test.*
- *Thus, the compound X must be a 2° alcohol, as only secondary alcohols give ketones on oxidation and hence, X is* $(CH_3)_2CHOH$.



40. I. CF_3OH is more acidic than CH_3OH because strong electron-withdrawing effects of the three fluorine atoms in CF_3-group delocalise the negative charge on oxygen.

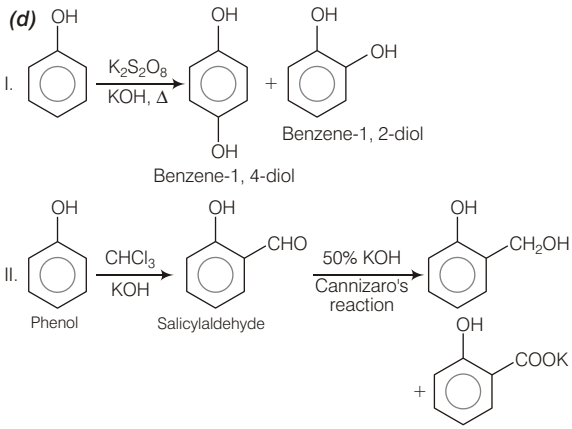
III. In oxymercuration-demercuration, product forms in accordance with Markownikoff's rule and without formation of carbocation. Thus, rearrangement does not occur.

41. ***(a)*** A-r, B-s, C-p, D-q.

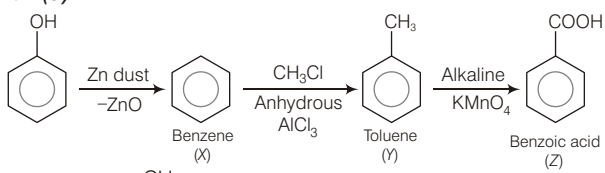
42. ***(a)*** The boiling point increases as the molecular mass of the alcohol increases. Further, among isomeric alcohols, 1° alcohols have higher boiling points than 2° alcohols. In other words, the boiling point increases in the following order: propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol.

I III II IV

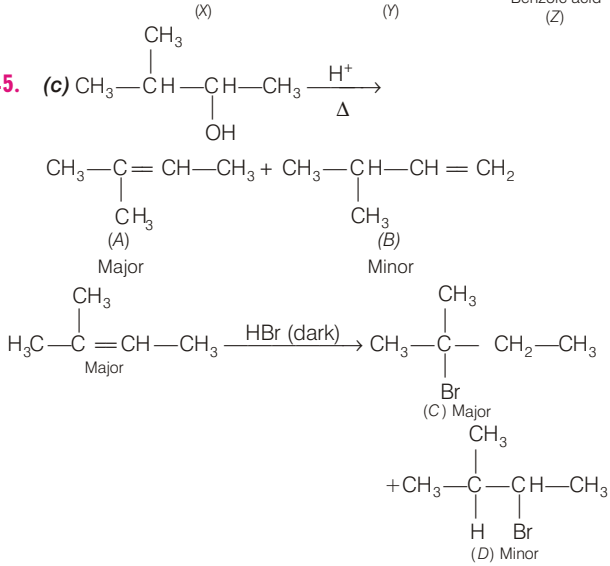
43. ***(d)***



44. ***(d)***



45. ***(c)***



To be Continued at Page 69

DO YOU KNOW?

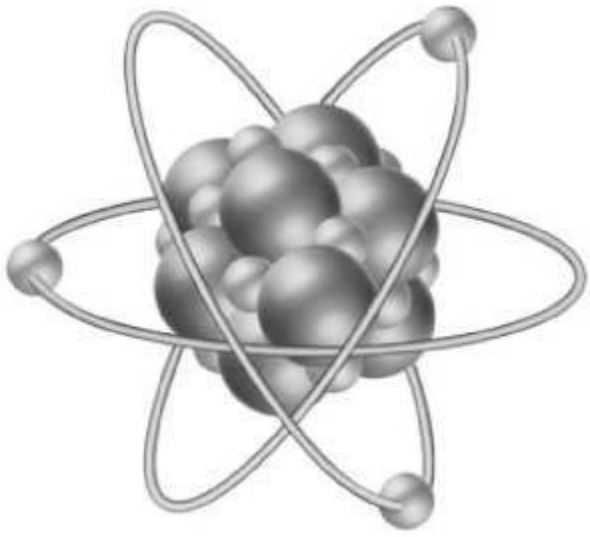
- **Why the metallic titanium is used in jet engines and other components of modern airplanes?**
  - The metallic titanium has an unusually high ratio of strength to weight. It is considerably stronger than either of aluminium or steel. Its density is intermediate between Al and Fe.
  - Titanium is extremely resistant to corrosion by air, soil, sea water and even reactive chemicals such as HNO_3 and Cl_2 gas. Like aluminium, it forms thin, tightly adherent oxide layer that protects the metal from further attack.
  - These properties of titanium make it useful in spacecraft of all types, it is widely used in jet engines and other components of modern airplanes.
  - Titanium and its compounds are nontoxic. These features account for the use of the metal in knee and hip replacements as well as dental implants. Thus, titanium is a metal of all purposes. Titanium has certain limitations. It is far more expensive than aluminium or steel, selling for about 700 rupees per kilogram. The high cost of extracting it from its ore (ilmenite) makes it very unlikely, that you rarely, have seen it in a machine used for cutting the grass on a lawn or kitchen sinks made out of titanium.
- **Why burn from steam is more painful than that from boiling water?**
  - Water turns into steam at 100°C. So, boiling water could not have temperature greater than 100°C, while steam can have temperature greater than 100°C. When steam hits on your skin, a lot of energy released as it condenses into liquid (undergoing a phase change). This energy causes more painful burn than if the same amount of boiling water hits on your skin. After hitting your skin, the temperature of boiling water would decrease to your skin's temperature but would not have undergo phase change.
  - The loss of energy that is released from steam hitting your skin occurs quickly and in a small localised area, therefore causing damage to your cells.
- **Group 2 metal ions also form coordination compounds.**
  - The group 2 metal ions (M^{2+}) are smaller and have twice the charge than that of group1 metal ions (M^{+}). This means that electron densities on group 2 cations are much lower than those on group 1 cations. As a result group 2 coordination chemistry is more extensive than that of group 1. The most important ligands are those with oxygen and nitrogen donor atoms.
  - The increasing size of the M^{2+} ions down the group influences the coordination number, which is the number of atoms that are coordinated to metal ion. Be^{2+} typically has a coordination number of 4, Mg^{2+} has a coordination number of 6, whereas the coordination numbers of Ca^{2+}, Sr^{2+} and Ba^{2+} can be higher. Group 2 cations are strongly hydrated in aqueous solution, water molecules are coordinated to the cations,

$$[Be(H_2O)_4]^{2+}(aq) + H_2O(l) \rightleftharpoons [Be(H_2O)_3(OH)]^{+}(aq) + H_3O^{+}(aq)$$

  - The charge density on the small Be^{2+} cation is so large that in solution the ion is always coordinated and in aqueous solution it forms $[Be(H_2O)_4]^{2+}$ ions.
  - Unlike the other group 2 cations, solutions of Be^{2+} are acidic because of hydrolysis. The high charge density on the beryllium ion polarises the O—H bonds of the coordinated water molecules, so that H^{+} ions are more easily removed.
- **Low cost chemical sensors, made from chemically altered carbon nanotubes enable smart phones or other wireless devices to detect trace amounts of toxic gases.**
  - The researchers design light weight, inexpensive radiofrequency identification badges to be used for personal safety and security. Such badges could be worn by soldiers on the battlefield to rapidly detect the presence of chemical weapons, such as nerve gas or choking agents.
  - The sensor is a circuit loaded with carbon nanotubes, which are normally highly conductive but have been wrapped in an insulating material that keeps them in a highly resistive state. When exposed to certain toxic gases, the insulating material breaks apart and the nanotubes become significantly more conductive. This sends a signal that is readable by a smartphone with near-field communication technology, which allows devices to transmit data over short distances.
  - These sensors are sensitive enough to detect less than 10 parts per million of target toxic gases in about five seconds.
  - Moreover, the sensors each cost about a nickel to make; roughly 4 million sensors can be made from about 1 g of carbon nanotube materials. You really cannot make anything cheaper.
  - That's a way of getting distributed sensing into many people's hands.
  - These inexpensive, wireless sensors are called *chemiresistors,* that have detected spoiled meat and the ripeness of fruits.
  - All of these sensors are designed similarly, with carbon nanotubes that are chemically modified, so that their ability to carry an electric current changes when exposed to a target chemical.
  - This time, the researchers designed sensors highly sensitive to electrophiles, which are often toxic and used for chemical weapons.
  - According to the researchers, such a wireless system could be used to detect leaks of lithium thionyl chloride ($Li-SOCl_2$) batteries, which are used in medical instruments, fire alarms and military systems.

BOHR'S MODEL & HYDROGEN

FOR CLASS XI



This section of magazine is aimed to increase the connectivity between reader and NCERT Textbooks. Readers are advised to solve these questions with the help of references of NCERT books given at the end of the sections.

1. *A* in *B* was the first to explain quantitatively the general features of hydrogen atom structure and its spectrum. Choose an appropriate word to complete the statement.

(a) *A* → Rydberg; *B* → 1913
(b) *A* → Neil's Bohr; *B* → 1913
(c) *A* → de-Broglie; *B* → 1915
(d) *A* → Neil's Bohr; *B* → 1915

2. The electron in the hydrogen atom can move around the nucleus in a circular path of the fixed radius and energy. These are called *A*

Here *A* refer to

(a) orbits *(b)* orbitals
(c) circular paths *(d)* None of these

3. The energy of an electron in the orbit

(a) does not change with time
(b) changes with time
(c) sometimes change and sometimes not
(d) None of the above

4. Consider the following statements.

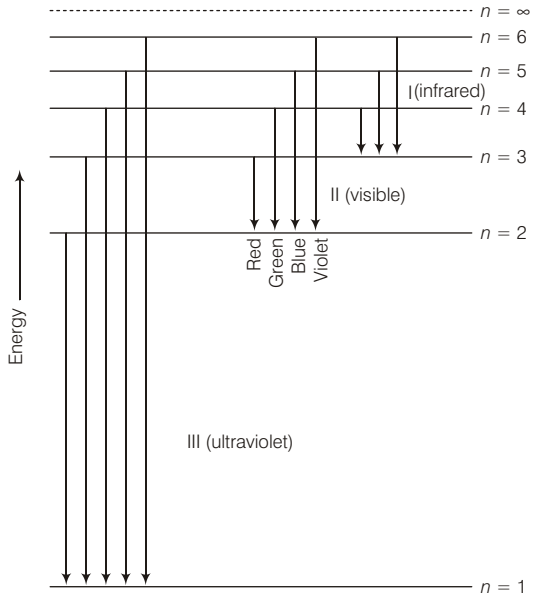
I. The Lyman series is observed in ultraviolet region.
II. The Brackett series is observed in visible region.
III. The Pfund series is observed in infrared region.
IV. The Balmer series is observed in infrared region.

Mark the above statements as true and false and choose the correct option.

	I	II	III	IV
(a)	T	F	T	F
(c)	T	T	F	F

	I	II	III	IV
(b)	F	T	F	T
(d)	F	T	T	F

5. Transition of the electron in the hydrogen atom is shown in the given figure.



Identify I, II, III in the above figure.

	I	II	III
(a)	Lyman series;	Paschen series;	Balmer series
(b)	Paschen series;	Lyman series;	Balmer series
(c)	Paschen series;	Balmer series;	Lyman series
(d)	Balmer series;	Lyman series;	Paschen series

6. Consider the following statements.

I. According to Bohr's postulate, 'the energy change does not take place in a continuous manner with in the orbit.'

II. Angular momentum is the product of inertia (I) and angular velocity (ω).

III. Linear momentum is the product of mass(m) and linear velocity (v).

Select the correct statement(s) and mark the correct option.

(a) Only I (b) II and III
(c) I and IV (d) All are correct

7. Which of the following expression is commonly known as Bohr's frequency rule?

(a) $v = \Delta E \cdot h = (E_2 - E_1)h$

(b) $v = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$

(c) $\frac{v}{h} = \Delta E + h = (E_2 - E_1) + h$

(d) $v = \frac{\Delta E}{2} = \frac{E_1 - E_2}{2}$

8. The angular momentum of an electron in a given stationary state can be expressed as

(a) $\frac{M_e v}{r} = n \cdot \frac{h}{2\pi}$; $(n = 1, 2, 3 \ldots)$

(b) $M_e vr = n \cdot \frac{h}{2\pi}$; $(n = 1, 2, 3 \ldots)$

(c) $M_e v = \frac{nhr}{2\pi}$; $(n = 1, 2, 3 \ldots)$

(d) $M_e vr = \frac{h}{2\pi n}$; $(n = 1, 2, 3 \ldots)$

9. The stationary states for an electron are numbered $n = 1, 2, 3 \ldots$ .These integral numbers are known as A. Here A refers to

(a) azimuthal quantum number
(b) principal quantum number
(c) spin quantum number
(d) None of the above

10. Which of the following is the correct expression for 'radii' of the stationary states?

(a) $r_n = n^2 a_0$ (b) $r_n = n^2 + a_0$
(c) $r_n = n^2 - a_0$ (d) $r_n = \frac{n^2}{a_0}$

11. Consider the following statements.

I. The value of a_0 in $r_n = n^2 a_0$ is 52.9 nm.

II. The radius of the first stationary state is called Bohr's radius.

III. An electron can move only in those orbits for which its angular momentum is integral multiple of $\frac{h}{2\pi}$.

Select the correct statement(s) and mark the correct option

(a) Only I (b) II and III
(c) I and III (d) All are correct

12. The most important property associated with the electron, is the energy of its stationary state. It is given by the expression

(a) $E_n = R_H n^2$; $(n = 1, 2, 3 \ldots)$

(b) $E_n = -R_H n^2$; $(n = 1, 2, 3 \ldots)$

(c) $E_n = R_H\left(\frac{1}{n^2}\right)$; $(n = 1, 2, 3 \ldots)$

(d) $E_n = -R_H\left(\frac{1}{n^2}\right)$; $(n = 1, 2, 3 \ldots)$

13. In expression $E_n = -R_H\left(\frac{1}{n^2}\right)$, $(n = 1, 2, 3 \ldots)$, R_H is called …A… and its value is …B… . The energy of the lowest state also called …C… . Here A, B, C, respectively are

(a) Rydberg constant ; 2.18×10^{-18} J ; Ground state
(b) Bohr constant ; -2.18×10^{-18} J ; First state
(c) Rydberg constant ; -2.18×10^{-18} J ; Last state
(d) Bohr constant ; 2.18×10^{-18} J ; Lower state

14. Consider the following statements.

I. Energy of electron in the orbit is quantised.

II. Angular momentum of the electron in the orbital is quantised.

III. Energy of electron decreases with increase in the value of principle quantum number.

Select the correct statement(s) and mark the correct option.

(a) Only I (b) I and II
(c) II and III (d) I, II and III

15. The energy of the electron in a hydrogen atom has a negative sign because

(a) the energy of the electron in the atom is lower than the energy of a free electron at rest
(b) the energy value assigned to free electron at rest is zero
(c) a free electron at rest is an electron that is infinitely far away from the nucleus
(d) (a), (b) and (c) together forms the valid reason for the given fact

16. When the electron is free from the influence of nucleus, the energy is taken as A.

Here, A refer to

(a) zero (b) one
(c) infinity (d) negative value

17. For an ionised hydrogen atom, value of principal quantum number is

(a) $n = 1$ (b) $n = 0$
(c) $n = \infty$ (d) $n \leq 1$

18. Bohr's theory can be applied to
(a) He^+ *(b)* Li^{2+} *(c)* Be^{3+} *(d)* All of these

19. The energies of the stationary states associated with hydrogen like species are given by the expression
(a) $E_n = -2.18 \times 10^{-18}\left(\frac{Z^2}{n^2}\right)$ J
(b) $E_n = 2.18 \times 10^{-18}\left(\frac{Z^2}{n^2}\right)$ J
(c) $E_n = 2.18 \times 10^{-18}\left(\frac{n^2}{Z^2}\right)$ J
(d) $E_n = -2.18 \times 10^{-18}\left(\frac{n^2}{Z^2}\right)$ J

20. Consider the following statements.
I. The radii of hydrogen like species can be expressed as, $r_n = \frac{52.9(n^2)}{Z}$ pm.
II. Qualitatively, the magnitude of velocity of electron increases with increase of positive charge on the nucleus.
III. The value of the energy of hydrogen like species becomes more negative and that of radii becomes smaller with increase of Z.
IV. Magnitude of velocity of electron decreases with increase of principal quantum number.
Select the correct statement(s) and mark the correct option.
(a) Only I
(b) I and II
(c) III and IV
(d) All are correct

21. The wave number $\bar{\nu}$ associated with the absorption and emission of the photon can be evaluated by using equation
(a) $\bar{\nu} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$ *(b)* $\bar{\nu} = -\frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$
(c) $\bar{\nu} = \frac{R_H \cdot h}{c}(n_i^2 - n_f^2)$ *(d)* $\bar{\nu} = -\frac{R_H \cdot h}{c}(n_i^2 - n_f^2)$

22. The brightness or intensity of spectral lines depends upon the
(a) number of photons of same frequency absorbed
(b) number of photons of same wavelength
(c) number of photons of same frequency emitted
(d) All of the above

23. The energy associated with the first orbit of Li^{3+} is
(a) -19.62×10^{-18} J
(b) 19.62×10^{-18} J
(c) 2.4×10^{-19} J
(d) -2.4×10^{-19} J

24. The radius associated with the first orbit of Li^{3+} is
(a) 0.01763 nm *(b)* 1.763 nm
(c) 17.63 nm *(d)* 176.3 nm

25. The first line in the Balmer series in the H-atom will have the frequency
(a) 8.02×10^{14} sec^{-1} *(b)* 4.57×10^{14} sec^{-1}
(c) 3.29×10^{15} sec^{-1} *(d)* 8.22×10^{15} sec^{-1}

26. The first line in the Lyman series in H-atom will have the wave number
(a) 8.23×10^{6} m^{-1} *(b)* 8.23×10^{22} m^{-1}
(c) 4.57×10^{14} m^{-1} *(d)* 3.29×10^{15} m^{-1}

27. A photon is emitted during a transition from $n = 5$ state to the $n = 3$ state in the hydrogen atom.
Consider the following statements regarding the above information.
I. The transition give rise to a spectral line in the IR region of the Paschen series.
II. The frequency of the photon is 2.3×10^{13} Hz.
III. The wavelength of the photon is 1304 nm.
IV. Its emission energy is 1.55×10^{-19} J.
Select the correct statement(s) and mark the correct option.
(a) Only I *(b)* II and III
(c) III and IV *(d)* All are correct

28. Consider the following statements.
I. Bohr's model fails to account for the finer details of the hydrogen atom spectrum observed.
II. Bohr's model is unable to explain the spectrum of atoms to form molecules by chemical bonds.
III. Bohr's model could not explain the ability of atoms to form molecules by chemical bonds.
Which of the above statement(s) is/are the limitations of Bohr's model?
(a) Only I *(b)* II and III
(c) I and II *(d)* All statements are correct

29. The phenomenon of splitting of spectral lines under the influence of the electric field is called .....
(a) stark effect
(b) zeeman effect
(c) photoelectric effect
(d) electromagnetic effect

30. The phenomenon of splitting of spectral lines under the influence of the magnetic field is called.....
(a) zeeman effect
(b) stark effect
(c) photoelectric effect
(d) electromagnetic effect

To be Continued at Page 75

PERIODIC PROPERTIES

FOR CLASS XI

Topicwise Collection of best subjective problems

Very Short Answer Type Questions [1 Mark]

1. How does screening constant 'σ' varies across the elements of 2nd period?
2. Give the correct decreasing order of ionic radius of H, H^+ and H^-.
3. Give the correct decreasing order of first ionisation potential of elements K, Ca, Rb and Cs.
4. Which element among strontium, magnesium, potassium and lithium is most reactive?
5. Which one of the following element will form the most acidic oxide? [HOTS]

   N, Al, Zn, Cl
6. Give the name of the elements having highest and lowest density, respectively.
7. Why sodium cannot exhibit + 2 oxidation state?
8. Among alkali metals which element do you expect to be least electronegative?
9. Why Be and Mg have zero value of electron affinity.
10. Which alkali metal is better reducing agent in aqueous medium?

Short Answer Type Questions [2 Marks]

11. Arrange the following isoelectronic species in the decreasing order of their ionic radii.

    F^-, O^{2-}, Na^+, Mg^{2+}
12. For a given orbit, how does the shielding power of electrons belonging to different subshell (*s, p, d, f*) varies?
13. Although first ionisation energy generally increases on moving across a period. Give reason, why this trend is not followed while comparing the ionisation energies of IIA, with IIIA group elements and VA with VIA group elements. [HOTS]
14. Why alkaline earth metals are diamagnetic?
15. Predict the nature of bond between two atoms *A* and *B*, if
    (a) there is a greater difference in the electronegativity of elements *A* and *B*.
    (b) the electronegativities of *A* and *B* are equal.

Short Answer Type Questions [3 Marks]

16. Why the atomic radius of fluorine is smaller than that of neon?
17. The ionisation energy of Na is 513 kJ mol^{-1}. Calculate the amount of energy required to convert 460 mg of Na-atoms into gaseous Na^+ ion.
18. Why $PbCl_4$ is a better oxidising agent while $GeCl_2$ is a better reducing agent? [HOTS]

Long Answer Type Questions [5 Marks]

19. Discuss Pauling scale for calculating electronegativity (χ) of an element. Use it to calculate the electronegativity of hydrogen from the following data. [HOTS]
    $E_{H—H}$ = 104.2 kcal mol^{-1}, $E_{C—C}$ = 83.1 kcal mol^{-1}, $E_{C—H}$ = 98.8 kcal mol^{-1}, χ_C = 2.6.
20. Explain diagonal relationship between alkali and alkaline earth metal.

Solutions

1. The magnitude of screening constant 'σ' increases across a period due to increase in the number of inner electrons.

2. Since, the radius of cation is always smaller than that of a neutral atom and the radius of anion is always greater than cation thus, the correct decreasing order of ionic radius of the given species is

$$H^- > H > H^+$$

3. Ionisation potential $\propto \frac{1}{\text{atomic size}}$.

As the atomic size increases down the group but decreases along a period, so the correct decreasing order of first ionisation potential is Ca > K > Rb > Cs.

4. Potassium is most reactive among the given metals as reactivity of metals decreases along a period and increases on moving down the group.

5. On moving from left to right in a period, acidic character of oxides increases. Thus, oxide of chlorine (Cl) will be most acidic among the given elements.

6. Density of osmium (Os) is the highest and that of hydrogen (H_2) is lowest among all the known elements.

7. Second ionisation potential of sodium (Na) is extremely high because after the removal of one electron, inert gas configuration is obtained. As a result sodium cannot show an oxidation state of +2.

8. On moving down the group, electronegativity decreases because atomic size increases. Francium (Fr) has the largest size, therefore it is least electronegative.

9. This is because Be and Mg have stable ns^2 configurations in their outermost shells.

10. Due to smaller size, of Li^+, it has higher charge density which leads to more negative hydration energy resulting in a more negative electrode potential, hence making Li a better reducing agent in an aqueous medium.

11. For isoelectronic species,

Ionic radius $\propto \frac{1}{\text{atomic number}}$

Since, atomic number increases as follows

$$O^{2-} > F^- > Na^+ > Mg^{2+}$$

Atomic number (8) (9) (11) (12)

Thus, the correct ionic radii orders is :

$$O^{2-} > F^- > Na^+ > Mg^{2+}$$

12. Shielding power of a subshell depends on its shape. *s*-orbital being spherical in shape shields the electrons in the outermost orbit from nuclear attractive force to the greatest extent. *p*-orbital being dumb-bell in shape, shields less than *s*-orbital, *d* and *f*-orbitals are even more diffused and their electron density is located at farther place from the nucleus, hence, shielding power of electrons belonging to different subshells decreases in the order.

$$s > p > d > f$$

13. Due to the presence of fully filled *s*-orbitals in case of group (IIA) elements (their outermost electronic configuration is ns^2) and a stable half-filled electronic configuration of group (VA) elements, their ionisation energies are greater than the elements of the succeeding groups, i.e. (IIIA) and (VIA), respectively.

14. If a substance has all paired electrons then these electrons are repelled by applied magnetic field and such substance is called diamagnetic.

Electronic configuration of valence shell of alkaline earth metal is ns^2. Thus, they do not have any unpaired electron and are diamagnetic.

15. (a) Greater the difference in the electronegativity of elements *A* and *B*, greater will be the ionic character of bond between *A* and *B*.

(b) If electronegativities of *A* and *B* are equal, the bond between *A* and *B* is supposed to be covalent.

16. Atomic radius of F is expressed in terms of covalent radius while atomic radius of neon is usually expressed in terms of van der Waals' radius. Since, van der Waals' radius of an element is always larger than its covalent radius, therefore, atomic radius of F is smaller than atomic radius of Ne (F = 72 pm, Ne = 160 pm).

17. Number of moles of Na $= \frac{\text{Mass (in g)}}{\text{Atomic mass (in g mol}^{-1})}$

$$= \frac{460 \times 10^{-3}\ \text{g}}{23\ \text{g mol}^{-1}}$$

$$= 2 \times 10^{-2}\ \text{mol}$$

$\because$ For the conversion of 1 mole atoms of Na into Na^+, the energy required = 513 kJ mol^{-1}.

$\therefore$ For the conversion of 2×10^{-2} mole atoms of Na into Na^+ ions, the energy required will be $513 \times 2 \times 10^{-2} = 10.26$ kJ.

18. Due to inert pair effect stabilities of

$$Pb^{4+} < Pb^{2+} \text{ and } Ge^{4+} < Ge^{2+}.$$

hence, $Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$

and $Ge^{2+} \longrightarrow Ge^{4+} + 2e^-$

are spontaneous towards more stable ions. Pb^{4+} can be easily reduced to Pb^{2+} and thus act as an oxidising agent, Ge^{2+} can be easily oxidised and thus, act as a reducing agent.

19. **Pauling Scale** The electronegativities are calculated with the help of bond energies.

If χ_A and χ_B are the electronegativities of two different elements *A* and *B*, then

$$\chi_A - \chi_B = 0.208\sqrt{\Delta}$$

where, $\Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$

E_{A-B}, E_{A-A} and E_{B-B} are the bond energies of the molecules *AB*, A_2 and B_2, respectively.

Calculation of electronegativity of hydrogen

$$\chi_C - \chi_H = 0.208\sqrt{\Delta}$$

$$\Delta = E_{C—H} - \sqrt{E_{C—C} \times E_{H—H}}$$

$$= 98.8 - \sqrt{83.1 \times 104.2}$$

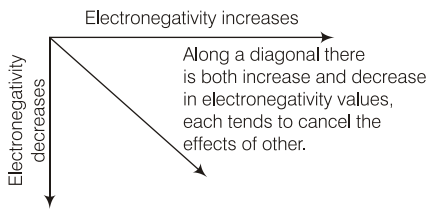
$$= 98.8 - 93.05 = 5.75$$

$$\therefore \quad \chi_C - \chi_H = 0.208\sqrt{5.75} = 0.498$$

$$\chi_H = \chi_C - 0.498 = 2.6 - 0.498$$

$$= 2.102 \approx 2.1$$

20. On moving one place to the right across a period, the increased nuclear charge holds the electrons more tightly to the atom. On moving down one place in a group, the extra shell of electrons decreases the attraction of nucleus for the outer electrons. A **diagonal** move means that these effects tend to compensate for one another. e.g. the electronegativity increases as we go from Li to Be but it decreases as we move from Be to Mg. As we move diagonally, these two effects partly cancel each other and there is no marked change in electronegativity. Thus, Li and Mg have close values of electronegativities. Because of this, Li and Mg show similarity in properties.


Electronegativity increases
Electronegativity decreases
Along a diagonal there is both increase and decrease in electronegativity values, each tends to cancel the effects of other.

TOUCH UP

CONDUCTANCE OF ELECTROLYTIC SOLUTION

FOR CLASS XII

Topicwise Collection of Best Subjective Problems

Very Short Answer Type Questions [1 Mark]

1. Give one main point of difference between metallic conductors and electrolytic conductors.
2. Why does the conductivity of a solution decreases with dilution?
3. Why alternating current is used for measuring resistance of an electrolytic solution? [HOTS]
4. If specific conductivity of $\frac{N}{50}$ KCl solution at 298 K is $0.002765\ \Omega^{-1}cm^{-1}$ and resistance of a cell containing this solution is 100 Ω, calculate the cell constant.
5. Give the expression for the conductance of a solution. Also write its unit.
6. How is degree of dissociation related to equivalent conductance at a given concentration?
7. If the equivalent conductance of 1M benzoic acid is $12.8\ ohm^{-1}cm^2eq^{-1}$ and if the conductances of benzoate ion and H^+ ions are 42 and $288.42\ ohm^{-1}cm^2eq^{-1}$, respectively. Calculate the degree of dissociation of benzoic acid.
8. The conductivity of 0.375 M solution of NaCN at 298 K is 0.0196 Scm^{-1}. Calculate its molar conductivity.
9. Equivalent conductance of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91 $ohm^{-1}cm^2eq^{-1}$, respectively.
   What would be the equivalent conductance of CH_3COOH at infinite dilution ?
10. State Kohlrausch law of independent migration of ions. [Delhi 2010]

Very Short Answer Type Questions [2 Marks]

11. Determine the relationship between molar conductance and equivalent conductance.
12. The resistance of decinormal solution of a salt occupying a volume between two platinum electrodes 2.10 cm apart and 3.6 cm^2 area was found to be 48 ohm. Calculate specific conductance and equivalent conductance.
13. Λ_{eq} of 0.10 N solution of CaI_2 is 100.05 cm^2eq^{-1} at 298K, cell constant of the cell is 0.25 cm^{-1}. How much current will flow when the potential difference between the electrode is 5V?
14. 0.1 M H_2SO_4 is diluted to 0.01 M H_2SO_4. Calculate the ratio of molar conductance at the two concentrations.
15. The conductivity of 0.001M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol. [Delhi 2008; All India 2016]

Short Answer Type Questions [3 Marks]

16. From the following molar conductivities at infinite dilution.
    Λ°_m for $Ba(OH)_2 = 457.6\ \Omega^{-1}cm^2\,mol^{-1}$
    Λ°_m for $BaCl_2 = 240.6\ \Omega^{-1}cm^2\,mol^{-1}$
    Λ°_m for $NH_4Cl = 129.8\ \Omega^{-1}cm^2\,mol^{-1}$
    Calculate Λ°_m for NH_4OH.
17. The electrical resistance of a column of 0.02M NaOH solution of radius 0.25cm and length 25 cm is 4.75×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.
18. The conductivity(κ) of a saturated solution of AgBr at 298 K is 5.8×10^{-6} Scm^{-1}. If Λ^+_{Ag} and $\Lambda^\circ_{Br^-}$ are 50 and 90 S $cm^2\,mol^{-1}$, respectively, calculate the solubility and K_{sp} of AgBr. [HOTS]

Long Answer Type Questions [5 Marks]

19. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration. [All India 2008; Delhi 2012]

20. The conductivity of NaCl at 298 K has been determined at different concentrations and the results are given below. [HOTS]

Concentration/(*M*)	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa / Sm^{-1}$	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $C^{1/2}$. Find the value of Λ°_m.

Solutions

1. **Metallic Conductors** Conduct electricity without the decomposition of substance.

Electrolytic Conductors Conduct electricity with the decomposition of the substance or electrolyte.

2. Conductivity of a solution decreases with dilution because the number of ions that carry current in a unit volume of solution always decreases with decrease in concentration.

3. Alternating current is used in electrolysis so that concentration of ions in the solution remains constant and exact value of resistance is measured.

4. $\text{Cell constant} = \dfrac{\text{Specific conductivity}}{\text{Conductance}}$

$= \text{Specific conductivity} \times \text{resistance}$

$= 0.002765\,\Omega^{-1}\,cm^{-1} \times 100\,\Omega$

$= 0.2765\,cm^{-1}$

5. Conductance (G) of a solution is given as

$$G = \kappa \times \frac{a}{l}$$

where, κ = conductivity (specific conductance)

a = area of cross-section of conductor

l = length of conductor

The SI unit of conductance is Siemens, represented by symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1}.

6. Degree of dissociation

$$(\alpha) = \frac{\text{Equivalent conductance at a given concentration } \Lambda_C}{\text{Equivalent conductance at infinite dilution } \Lambda_\infty}$$

$$\therefore \quad \alpha = \frac{\Lambda_C}{\Lambda_\infty}$$

7. $\underset{\text{Benzoic acid}}{C_6H_5COOH} \rightleftharpoons \underset{\text{Benzoate ion}}{C_6H_5COO^-} + H^+$

$\Lambda^\infty_{(\text{Benzoic acid})} = \Lambda^\infty_{(\text{Benzoate ion})} + \Lambda^\infty_{(H^+)} = 42 + 288.42$

$= 330.42\ ohm^{-1}cm^2eq^{-1}$

$\alpha = \dfrac{\Lambda_C}{\Lambda_\infty} = \dfrac{12.8}{330.42} = 0.0387$

Percentage dissociation $= 0.0387 \times 100 \approx 3.9\%$

8. Molar conductivity,

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0196\,Scm^{-1} \times 1000}{0.375\,mol\,cm^{-3}}$$

$= 52.27\,Scm^2\,mol^{-1}$

9. $\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COONa} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$

$= 91 + 426.16 - 126.45$

$= 390.71\,ohm^{-1}cm^2eq^{-1}$

10. According to Kohlrausch law, the limiting molar conductivity of an electrolyte is the sum of the individual contributions of the cation and the anion of the electrolyte.

e.g. $\Lambda^\circ_{m(NaCl)} = \Lambda^\circ_{Na^+} + \Lambda^\circ_{Cl^-}$

11. Molar conductivity of a solution is given by

$$\Lambda_m = \left(\frac{\kappa \times 1000}{M}\right) ohm^{-1}cm^2mol^{-1} \quad \text{...(i)}$$

Equivalent conductivity of a solution is given by

$$\Lambda_{eq} = \left(\frac{\kappa \times 1000}{N}\right) ohm^{-1}cm^2eq^{-1}$$

Normality (N) = n-factor $\times M$

= Total charge (cation or anion) $\times M$

$$\therefore \quad \Lambda_{eq} = \frac{\kappa \times 1000}{\text{Total charge (cation or anion)} \times M}$$

Substituting Λ_m from eq (i)

$$= \frac{\Lambda_m}{\text{Total charge (cation or anion)}}$$

$$\Rightarrow \quad \Lambda_m = \Lambda_{eq} \times \text{Total charge of cation (or anion)}$$

12. Given, $R = 48$ ohm, $l = 2.10$ cm, $a = 3.6\,cm^2$

$$\kappa = \frac{1}{R} \times \frac{l}{a} = \frac{1}{48} \times \frac{2.10}{3.6} = 0.01215\ Scm^{-1}$$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{0.01215 \times 1000}{0.1} = 121.5\ Scm^2eq^{-1}$$

13. $\Lambda_{eq} = \dfrac{\kappa \times 1000}{N}$, $\kappa = \dfrac{\Lambda_{eq} \times N}{1000} = \dfrac{100.05 \times 0.1}{1000} = 0.01005\,Scm^{-1}$

$G(\text{conductance}) = \dfrac{\kappa}{\text{Cell constant}} = \dfrac{0.010005}{0.25} = 0.04002\ ohm^{-1}$ or S

$$R = \frac{1}{\text{Conductance } (G)} = \frac{1}{0.04002} = 24.99 \text{ ohm}$$

$\text{Current in ampere} = \dfrac{\text{Potential difference}}{\text{Resistance}}$ {From ohm's law, $V = IR$}

$$I = \frac{V}{R} = \frac{5}{24.99} = 0.2001\,A$$

14. $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

$\dfrac{(\Lambda_m)_i}{(\Lambda_m)_f} = \dfrac{M_f}{M_i}$

$\dfrac{(\Lambda_m)_i}{(\Lambda_m)_f} = \dfrac{0.01}{0.1}$

$(\Lambda_m)_i = 0.1 \times (\lambda_m)_f$

$(\Lambda_m)_f = 10 \times (\lambda_m)_i$

$\dfrac{(\Lambda_m)_f}{(\Lambda_m)_i} = 10$

15. Molar conductivity at 0.001 M,

$$\Lambda_m^c = \frac{\kappa \times 1000}{C}$$

$$= \frac{4 \times 10^{-5} \times 1000}{0.001} \text{Scm}^2/\text{mol}$$

$$= 40 \text{ Scm}^2/\text{mol}$$

Degree of dissociation,

$$\alpha = \frac{\Lambda^c}{\Lambda^\infty} = \frac{40}{390} = 0.10256$$

For the dissociation of acetic acid, CH_3COOH

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Initial conc.	C	0	0
After time (t)	$(C - C\alpha)$	$C\alpha$	$C\alpha$

Dissociation constant,

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{C\alpha \cdot C\alpha}{C - C\alpha} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$K_a = \frac{0.001 \times (0.103)^2}{(1 - 0.103)}$$

$$= \frac{1.061 \times 10^{-5}}{0.897} = 1.18 \times 10^{-5}$$

16. $\Lambda_m^\circ [Ba(OH)_2] = \lambda^\circ_{Ba^{2+}} + 2\lambda_{OH^-} = 457.6 \text{ S cm}^2 \text{ mol}^{-1}$

$\Lambda_m^\circ (BaCl_2) = \lambda^\circ_{Ba^{2+}} + 2\lambda^\circ_{Cl^-} = 240.6 \text{ S cm}^2 \text{ mol}^{-1}$

$\Lambda_m^\circ (NH_4Cl) = \lambda^\circ_{NH_4^+} + \lambda^\circ_{Cl^-} = 129.8 \text{ S cm}^2 \text{ mol}^{-1}$

$$\Lambda_m^\circ (NH_4OH) = \Lambda_m^\circ (NH_4Cl) + 1/2\,\Lambda_m^\circ [Ba(OH)_2] - 1/2\,\Lambda_m^\circ [BaCl_2]$$

$$= 129.8 + 457.6/2 - 240.6/2$$

$$= 238.3 \text{ S cm}^2 \text{ mol}^{-1}$$

17. $\text{Area } (a) = \pi r^2 = 3.14 \times \left(\frac{0.25}{2}\right)^2$

$$= 0.0490 \text{ cm}^2$$

$$l = 25 \text{ cm}$$

$$R = \frac{\rho l}{a} \text{ or } \rho = \frac{Ra}{l}$$

$$= \frac{4.75 \times 10^3 \text{ ohm} \times 0.0490 \text{ cm}^2}{25 \text{ cm}}$$

$$= 9.31 \text{ ohm cm}$$

$$\text{Conductivity } (\kappa) = \frac{1}{\rho} = \left(\frac{1}{9.321}\right) \text{S cm}^{-1}$$

$$= 0.1074 \text{ Scm}^{-1}$$

$$\text{Molar conductivity } (\Lambda_m) = \frac{\kappa \times 1000}{M} \text{ cm}^2 \text{ L}^{-1}$$

$$= \frac{0.1074 \text{ Scm}^{-1} \times 1000 \text{ cm}^2 \text{ L}^{-1}}{0.02 \text{ molL}^{-1}}$$

$$= 5.37 \times 10^3 \text{ S cm}^2 \text{ mol}^{-1}$$

18. $\Lambda_m^\circ (AgBr) = \lambda^\circ_{Ag^+} + \lambda^\circ_{Br^-}$

$$= (50 + 90) \text{ Scm}^2 \text{ mol}^{-1}$$

$$= 140 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \quad \Lambda_m^\circ (AgBr) = \Lambda_m (AgBr) = \frac{\kappa \times 1000}{S}$$

$$140 \text{ S cm}^2 \text{ mol}^{-1} = \frac{5.8 \times 10^{-7} \times 10^3}{S}$$

$$\therefore \quad S = \frac{5.8 \times 10^{-7} \times 10^3}{140}$$

$$S = 0.04 \times 10^{-4} \text{ mol L}^{-1}$$

$$= 0.04 \times 10^{-4} \times M$$

[$\because$ Molar mass of AgBr = 108 + 80 = 188 gL^{-1}]

$$= 0.04 \times 10^{-4} \times 188 \text{ gL}^{-1}$$

$$S = 0.752 \times 10^{-3} \text{ gL}^{-1}$$

Now, $AgBr \longrightarrow Ag^+ + Br^-$

$$K_{sp} = S^2 = (0.04 \times 10^{-4})^2$$

$$K_{sp} = 1.6 \times 10^{-11} \text{ mol}^2 \text{ L}^{-2}$$

19. **Conductivity κ,** The inverse of resistivity is called conductivity. It is also known as the specific conductance. It can be defined as the conductance of a solution of 1 metre length with area of cross-section equal to 1 square metre.

Molar Conductivity Molar conductivity of a solution is the conductance of that volume of solution containing one mole of electrolyte, kept between two electrodes having separation of unit length between them and large cross-sectional area, so as to contain the electrolyte. In other words, molar conductivity is the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. It is denoted by Λ_m.

Variation of Conductivity and Molar Conductivity with Concentration Conductivity always decreases with decrease in concentration (i.e. with dilution) of both the strong and weak electrolytes. This is due to the fact that the number of ions that carry current in a unit volume of solution always decreases with decrease in concentration.

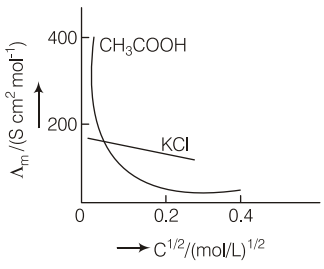
Conductivity is expressed as

$$G = \frac{\kappa A}{l} = \kappa$$

(both A and l are unity in their appropriate units in m or cm).

While molar conductivity is expressed as

$$\Lambda_m = \kappa V$$



Molar conductivity *versus* $C^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

It is because $\Lambda_m = \frac{\kappa A}{l}$

$\because \quad l = 1$ and $A = V$ [volume containing 1 mole of electrolyte]

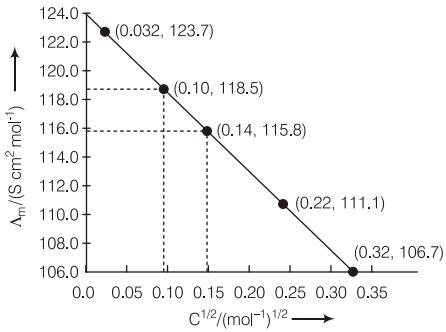
Therefore, $\Lambda_m = \kappa V$

Molar conductivity increases with decrease in concentration (i.e. with dilution). This is because the total volume V of solution containing one mole of electrolyte also increases.

20. According to the question, the given values are $1\ S\ cm^{-1} = 100\ S\ m^{-1}$ or $\frac{1\ S\ cm^{-1}}{100\ S\ m^{-1}} = 1$ [unit conversion factor]

Concentration (M)	κ ($S\ m^{-1}$)	κ (Scm^{-1})	$\Lambda_m = \frac{1000 \times \kappa}{\text{Molarity}}$ ($S\ cm^2\ mol^{-1}$)	$C^{1/2}$ ($M^{1/2}$)
10^{-3}	1.237×10^{-2}	1.237×10^{-4}	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.0316
10^{-2}	11.85×10^{-2}	11.85×10^{-4}	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
2×10^{-2}	23.15×10^{-2}	23.15×10^{-4}	$\frac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$	0.141
5×10^{-2}	55.53×10^{-2}	55.53×10^{-4}	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10^{-1}	106.74×10^{-2}	106.74×10^{-4}	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316

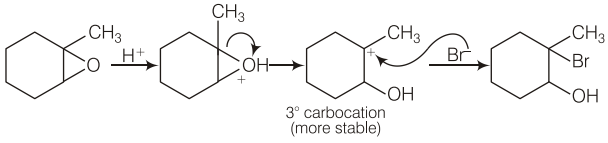
So, the graph between Λ_m and $C^{1/2}$ is shown below



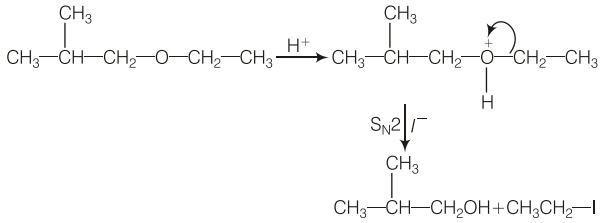
Λ° = Intercept on the Λ_m axis = 124.0 $S\ cm^2\ mol^{-1}$ (the value of Λ_m on extrapolation to zero concentration).

Continued from Page 59

46. ***(a)*** I. In acidic medium cleavage occurs by S_N1 mechanism as shown below



II. Nucleophilic attack occurs on the smaller alkyl group.



47. ***(d)*** **Short Trick**

The order of reactivity depends upon the stability of the carbocations formed,

Since, the relative stabilities of $FCH_2\overset{+}{C}HCH_3$, $FCH_2CH_2\overset{+}{C}HCH_3$, $CH_3\overset{+}{C}HCH_3$ and $Ph\overset{+}{C}H_2$. carbocations follow the order.

$Ph\overset{+}{C}H_2 > CH_3\overset{+}{C}HCH_3 > FCH_2CH_2\overset{+}{C}HCH_3 > FCH_2\overset{+}{C}HCH_3$,

therefore, the order of reactivity of the alcohols follows the sequence IV > III > II > I.

48. ***(b)***

I. NO_2 group does not show $-R$-effect at *m*-position, therefore, *m*-nitrophenol is the weakest acid. Due to intramolecular H-bonding, *o*-nitrophenol is less acidic than *p*-nitrophenol. Thus, the order is II > III > I.

II. In phenols, presence of electron withdrawing group increases the acidity whereas presence of electron releasing group decreases the acidity of phenol. Hence, the order of acidity is III > I > II.

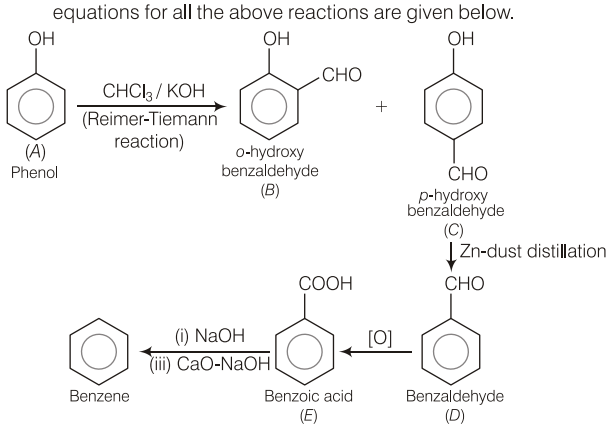
III. Due to strong-*I* and -*R*-effects of three —NO_2 groups, 2, 4, 6-trinitrophenol is more acidic than CH_3COOH. Further, due to greater resonance stabilisation of acetate ion over phenoxide ion, acetic acid is stronger acid than phenol. Hence, the order of acidity is II > I > III.

49. ***(a)*** Since, compound *A* on treatment with $CHCl_3$ and KOH (i.e. Reimer-Tiemann reaction), gives two products *B* and *C*. Therefore, *A* must be phenol and *B* and *C* must be *o*-hydroxybenzaldehyde and *p*-hydroxybenzaldehyde, respectively.

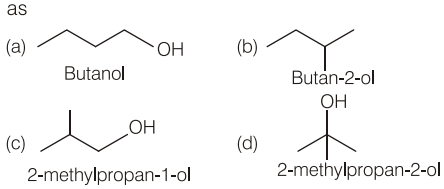
Since, both *B* and *C* on distillation with Zn dust give the same compound *D*, therefore, *D* must be benzaldehyde.

Since, oxidation of *D* gives *E* with $C_7H_6O_2$. Therefore, *E* must be benzoic acid.

(iv) Since, sodium salt of *E*, i.e. benzoic acid upon heating with soda-lime gives compound *F*, therefore *F* must be benzene. Zn-dust distillation of *A* would also give benzene *F*. The chemical equations for all the above reactions are given below.



50. ***(b)*** The possible structures of alcohols having formula C_4H_9OH are as



Among these, 2-methyl propan-2-ol cannot be prepared by the reduction of carbonyl compounds.

BRAIN TEASERS

To boost up your ranks in JEE Main and Advanced

1. When a certain metal was irradiated with light of frequency 3.2×10^{16} Hz, the photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted, when the same metal was irradiated with light of frequency 2.0×10^{16} Hz. Find the value of threshold frequency for the metal.

(a) 8×10^{15} Hz *(b)* 8×10^{14} Hz
(c) 8×10^{13} Hz *(d)* 8×10^{12} Hz

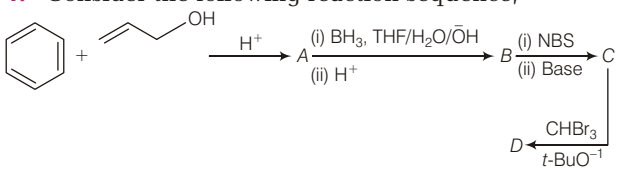
2. The specific conductivity of 0.02 M KCl solution at 25°C is $2.768 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$. The resistance of this solution at 25°C, when measured with a particular cell was 250.2 Ω. The resistance of 0.01 M $CuSO_4$ solution at 25°C measured with the same cell was 8331 Ω. Calculate the molar conductivity of the copper sulphate solution.

(a) $7.2\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ *(b)* $9.1\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$
(c) $8.3\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ *(d)* $2.7\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$

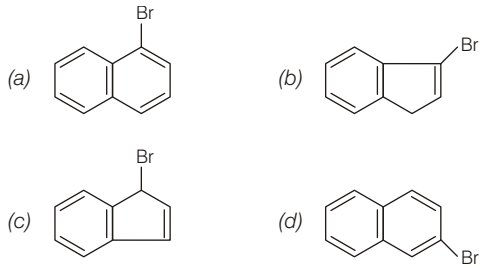
3. An optically active drug has one chiral center and only dextrorotatory isomer is effective. Moreover, it becomes ineffective when its optical activity is reduced to 35% of original. It was found that mutarotation of this drug was first order reaction with a rate constant of 10^{-8}s^{-1}. Find the expiration time of the drug in years.

(a) 4.07 *(b)* 3.03 *(c)* 2.00 *(d)* 1.36

4. Consider the following reaction sequence,



Which of the following is the structure of compound *D*?



5. A graph between $\log\left(\frac{x}{m}\right)$ *versus* $\log p$ was found to be linear with slope of 45° and intercept of 0.3010. The amount of the gas adsorbed per gram of charcoal under a pressure of 0.5 atm is

(a) 1.0 *(b)* 2.0 *(c)* 3.0 *(d)* 4.0

6. Consider the following statements about plots of $\Delta_f G$ *versus* T, for ease of reduction of ores. Choose the incorrect statement among the following.

(a) In the formation of metal oxide, slope of curve comes out to be positive
(b) For some reactive metals, $\Delta G°$ becomes zero at high temperature
(c) For CO, slope of curve comes out to be in upward direction
(d) Decreasing order of reducing power of different metals is:
Ca > Mg > Al > Cr > Zn > Fe > Ni

7. Which of the following reactions is incorrect for potassium dichromate?

(a) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$
(b) $3SO_3^{2-} + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$
(c) $K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \xrightarrow{\text{Ether}} K_2SO_4 + 2CrO_5 + 5H_2O$
(d) $2K_2Cr_2O_7 + 2K_4[Fe(CN)_6] \longrightarrow 2K_2O + 2Cr_2O_3 + 6KCN + 3O_2 + K_2Fe[Fe(CN)_6]$

8. An organic compound, *A* on treatment with ethyl alcohol gives a carboxylic acid *B* and compound *C*. Hydrolysis of *C* under acidic conditions gives *B* and *D*. Oxidation of *D* with $KMnO_4$ also gives *B*. *B* on heating with $Ca(OH)_2$ gives *E* (C_3H_6O). *E* does not give Tollen's test and does not reduce Fehling's solution but form a 2, 4-dinitrophenyl hydrazone. Identify the structure of *E*.

(a) CH_3COOH *(b)* CH_3COCH_3
(c) CH_3CHO *(d)* HCOOH

9. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mole of He and 1.0 mole of an unknown compound (vapour pressure 0.68 atm at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is

(a) 7 L *(b)* 6 L
(c) 5 L *(d)* 4 L

10. 20 mL of an alkali solution was added to a 50 mL solution of a weak monobasic acid H*A* and pH of the solution was found to be 4.5. To the above solution 30 mL of the same alkali was further added and pH of the final solution was found to be 5.2. Find the value of dissociation constant (K_a) of acid.

(a) 1.05×10^{-4} *(b)* 1.68×10^{-4}
(c) 1.05×10^{-5} *(d)* 1.68×10^{-5}

Answers with Explanation

1. ***(a)*** According to photoelectric effect equation,

$$KE = h\nu - h\nu_0$$

or $$(\nu - \nu_0) = \frac{KE}{h}$$

Given, $\nu_1 = 3.2 \times 10^{16}$ Hz,

$\nu_2 = 2.0 \times 10^{16}$ Hz, $KE_1 = 2KE_2$

Now, $$\nu_2 - \nu_0 = \frac{KE_2}{h} \quad \ldots(i)$$

$$\nu_1 - \nu_0 = \frac{KE_1}{h} \quad \ldots(ii)$$

Dividing Eq. (ii) by Eq. (i), we get

$$\frac{\nu_1 - \nu_0}{\nu_2 - \nu_0} = \frac{KE_1}{KE_2} = \frac{2KE_2}{KE_2} = 2 \qquad [\because KE_1 = 2KE_2]$$

or $$\nu_1 - \nu_0 = 2\nu_2 - 2\nu_0$$

or $$\nu_1 - 2\nu_2 = -\nu_0$$

or $$\nu_0 = 2\nu_2 - \nu_1$$
$$= 2(2 \times 10^{16}) - (3.2 \times 10^{16})$$
$$= 8 \times 10^{15} \text{ Hz}$$

2. ***(c)*** Cell constant is given as,

$$\text{Cell constant} = \frac{\text{Specific conductivity of KCl}}{\text{Conductance of KCl}}$$
$$= \frac{2.768 \times 10^{-3}}{1/250.2}$$
$$= 2.768 \times 10^{-3} \times 250.2$$

For 0.01 M $CuSO_4$ solution,

Specific conductivity = Cell constant × conductance

$$= 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$$

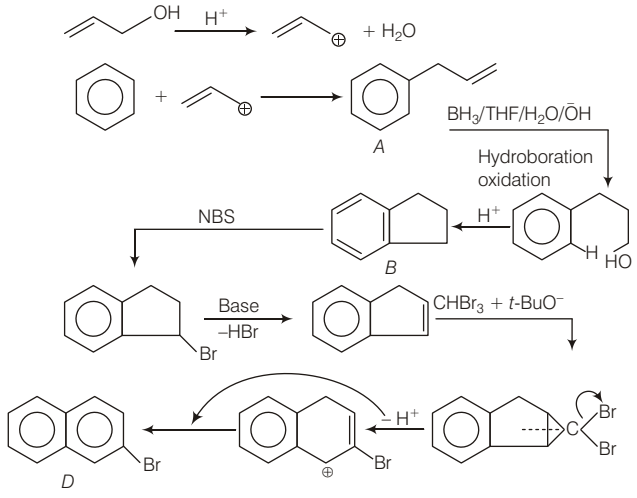
$$\text{Molar conductance} = \text{Specific conductivity} \times \frac{1000}{C}$$
$$= \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100}$$
$$= 8.313\,\Omega^{-1}\text{cm}^2\,\text{mol}^{-1}$$

3. ***(d)*** The optical activity remained = 35%.

So, 65% optical activity has been lost. It means 35% of dextrorotatory isomer has been converted to laevorotatory isomer. Applying integrated rate law for first order reaction,

$$2.303 \log \frac{100}{65} = 1 \times 10^{-18} \times t$$
$$t = 4.31 \times 10^7 \text{s}$$
$$1 \text{ yr} = 365 \times 24 \times 60 \times 60 \text{ s}$$
$$= 3.153 \times 10^7 \text{s} = 1.36 \text{ yr}$$

4. ***(d)***



5. ***(a)*** According to Freundlich equation,

$$\frac{x}{m} = K(p)^{1/n}$$

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log p \quad \ldots(i)$$

On comparing above equation with linear equation $y = mx + c$

$$m = \text{slope} = \frac{1}{n}$$

and c = Intercept = log K

Thus, $\frac{1}{n} = \tan\theta = \tan 45° = 1$ or $n = 1$

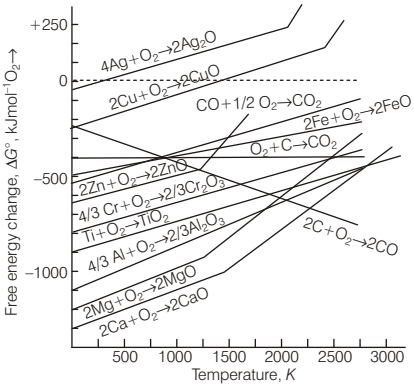
$\therefore$ log K = 0.3010 [Given]

or K = antilog (0.3010) = 2

At p = 0.5 atm

$$\frac{x}{m} = K(p)^{1/n} = 2 \times (0.5)^1 = 1.0$$

6. ***(c)*** All the statements given in the problem are about Ellingham's diagrams.

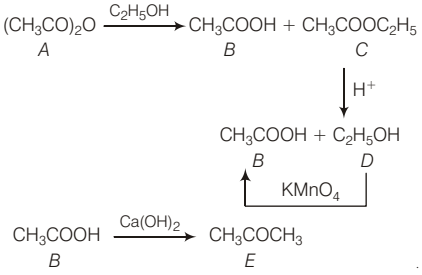


For CO, slope of curve is downward, because with rise in temperature $\Delta S°$ increases and value of $\Delta G°$ becomes more negative.

7. ***(d)*** On fusion with dry $K_4[Fe(CN)_6]$, potassium cyanate is formed.

$$2K_2Cr_2O_7 + 2K_4[Fe(CN)_6] \longrightarrow 2K_2O + 2Cr_2O_3 + \underset{\text{Potassium cyanate}}{6KCNO} + K_2Fe[Fe(CN)_6]$$

8. ***(b)***



9. ***(a)*** Given, p_{ext} = 1 atm, number of moles of He; (n_{He}) = 0.1,

Number of moles of unknown compound, n_{uc} = 1

Vapour pressure of unknown compound = 0.68 atm

$\because$ External pressure is 1.0 atm therefore, the gas pressure is also 1.0 atm.

$\therefore$ Partial pressure of He = Total pressure – pressure of unknown compound = (1 – 0.68) atm = 0.32 atm

$$\text{Volume of gases at 0°C} = \frac{n_{He} \times R \times T}{p_{He}}$$

$$= \frac{0.1\,\text{mol} \times 0.082\,\text{atm L mol}^{-1}\,\text{K}^{-1} \times 273\,\text{K}^{-1}}{0.32\,\text{atm}} = 6.99\,\text{L} \simeq 7\,\text{L}$$

Volume of container = Volume of He

10. ***(c)*** In both cases the solution is acidic as pH is less than 7 in both cases.

$$\underset{\text{Monobasic acid}}{HA} \rightleftharpoons H^+ + A^- \quad \ldots(i)$$

$$\underset{\text{Alkali}}{NaOH} \rightleftharpoons Na^+ + \bar{O}H \quad \ldots(ii)$$

Let 20 mL alkali contains x mol of base and 50 mL of acid solution nitially contains y mol of acid

After the addition of 20 mL of alkali,

$$HA + NaOH \rightleftharpoons Na^+ + A^- + H_2O$$

Moles of the salt = x

Moles of acid left = $y - x$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

or $$4.5 = pK_a + \log \frac{x}{y - x} \quad \ldots(i)$$

After further addition of 30 mL alkali,

Moles of salt = 2.5x

Moles of acid left = $y - 2.5x$

or $$5.2 = pK_a + \log \frac{2.5x}{y - 2.5x} \quad \ldots(ii)$$

Subtracting Eq. (i) from Eq. (ii), we get

$$0.7 = \log \frac{2.5x\,(y - x)}{(y - 2.5x)x}$$

or $$\frac{2.5\,(y - x)}{y - 2.5x} = \text{antilog}\,(0.7) = 5$$

or $$y = 4x$$

Substituting $y = 4x$ in Eq. (i), we get

$$4.5 = pK_a + \log \frac{x}{3x}$$

or $$4.5 = pK_a - \log 3$$

or $$pK_a = 4.977 \quad [\log 3 = 0.4771]$$

or $$-\log K_a = 4.977$$

or $$\log K_a = -4.977$$

or $$K_a = \text{antilog}\,(-4.977)$$

or $$K_a = 1.05 \times 10^{-5}$$

INSPIRING ICONS

Neeraj Kumar Mehra from Rajasthan, whose mother is a daily wage earner and earns Rs 150 by toiling in the fields. While she doesn't have a clue that IITs exist, her son is getting ready to take admission in the electrical branch of the coveted IIT Delhi. His father died a long time back. Due to his poor financial condition, he didn't even have a single mobile phone (something that most of us can't even think of).

He got an all India SC rank of 1443; he had opted to write his papers in Hindi. Now, he is focusing on improving his English.

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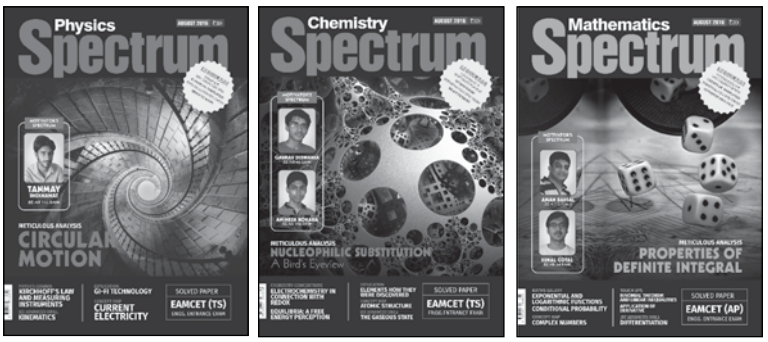

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CHEMISTRY @ SPECTRUM FOR YOU

In this section, we invite our readers to send their problems and we will try to provide the best possible solutions given by our expert panel.

Q1 Sir, I have read that radiocarbon dating is used in the determination of age of organic materials. If this method is useful to date ancient rocks, if not then explain me, which method is used?

[Aryan Kumar, Meerut]

- Aryan, radiocarbon dating is not used to date ancient rocks because half-life of ^{14}C is 5730 yrs. Thus, it is useful for samples upto about 100,000 yrs old not for samples of millions or billions of years old.

  To date ancient rocks, another radioactive isotope, ^{40}K, is used. ^{40}K is a radioactive isotope of potassium that is present as a relatively low concentration (0.0117%) of naturally occuring potassium. Unlike ^{14}C, ^{40}K has a half-life of 1.277×10^9 yrs and two main decay pathways. Through one pathway (β-emission), ^{40}K produces ^{40}Ca and through another pathway (electron capture) it gives ^{40}Ar

  β-emission $\quad {}^{40}_{19}K \longrightarrow {}^{40}_{20}Ca + {}^{0}_{-1}e$

  Electron capture $\quad {}^{40}_{19}K + {}^{0}_{-1}e \longrightarrow {}^{40}_{18}Ar$

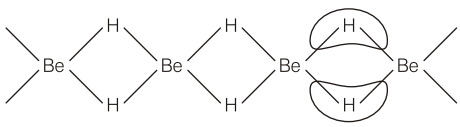
  Electron capture involves a reaction between the nucleus and a core electron in which a proton is converted to a neutron. Geologists determine the date of rocks by comparing the ratio of ^{40}K to ^{40}Ar. Potassium to argon dating has been used to date early hominid fossils in East Africa.

  Argon-argon dating is related but much more accurate dating technique. Samples of rock are irradiated with neutrons to convert ^{40}K into ^{39}Ar. ^{39}Ar is not a naturally occuring isotope of argon. The ratio of ^{40}Ar to ^{39}Ar is then determined by mass spectroscopy. Argon-argon dating is used for much smaller samples-milligrams rather than tens of grams. But this technique can be used accurately on samples only 2000 yrs old.

Q2 Sir, I have doubt regarding the structure of BeH_2. We know that, it exists in polymeric form. This polymeric form contains two bridged hydrogen atoms. Each of these two bridged hydrogen atoms forms two covalent bonds with two beryllium atoms, i.e. one bridged hydrogen atom has four electrons. How is this possible as hydrogen atom can accommodate maximum two electrons only? Please explain.

[Kavita, Jaipur]

- You have asked a very good question, Kavita. This doubt can come in the mind of any student. In order to clear your doubt, lets first look at the structure of polymeric BeH_2.



$(BeH_2)_n$ is a covalent and polymeric compound. Be is bonded to four H-atoms, and the H-atoms at bridges appear to form two bonds. Since, Be has two valence

electrons, and H only one, it is apparent that there are not enough electrons to form the usual electron pair bonds in which two electrons are shared between two atoms. Instead of this, three centre bonds are formed in which a banana-shaped molecular orbital (or three centre bond) covers three atoms (Be-----H----Be), and contains two electrons. This is called a three - centre two electron bond). This is an example of a cluster compound, where the monomeric molecule BeH_2 would result in only four electrons in the outer shell of the beryllium atoms. This situation is termed as electron deficient and by clustering, each atom shares its electrons with several neighbours and receives a share in their electrons.

Q3 **Sir, CH_3CH_2OH readily reacts with HBr and forms CH_3CH_2Br but it does not react with NaBr. Why?**

[Sumit Negi, Rishikesh]

- Sumit, reaction between CH_3CH_2OH and HBr follows S_N2 mechanism. In S_N2 mechanism, a stronger nucleophile displaces a weaker nucleophile. Now come to your question.

In case of the reaction between CH_3CH_2OH and NaBr, Br^- acts as a weaker nucleophile. Hence, Br^- could not displace a better nucleophile, $\bar{O}H$, therefore reaction does not occur.

In case of the reaction between CH_3CH_2OH and HBr, CH_3CH_2OH gets protonated first and forms $CH_3CH_2\overset{+}{O}H_2$. In this case, Br^-displaces the weaker nucleophile H_2O. Thus, reactions in both of the cases are given as,

(I) $CH_3CH_2OH + NaBr \longrightarrow$ No reaction

(II) $CH_3CH_2OH + HBr \longrightarrow CH_3CH_2\overset{+}{O}H_2 + Br^-$

$$Br^- + CH_3CH_2\overset{+}{O}H_2 \longrightarrow CH_3CH_2Br + H_2O$$

Q4 **Dear Sir, why cycloalkanes are more reactive as compare to the alkanes?**

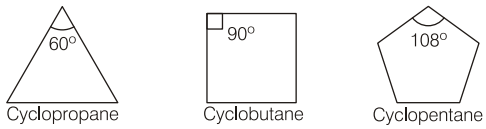
[Kusum Verma, Kanpur]

- Kusum, this can be explained by Baeyer's strain theory, according to which when an alkane having normal carbon tetrahedral bond angle 109°28′ is converted into cyclic compound a definite distortion of this normal angle takes place leading to the development of a strain in the molecule. Hence, greater the deviation from the normal angle (109°28′), greater will be the strain in the molecule which results greater unstability of the molecule. You can calculate angle strain of deviation (δ) from the following formula.

$$\delta = \frac{1}{2}(109°28' - \alpha)$$

α = Bond angle of cycloalkane.

e.g.



$$\delta = \frac{109°28' - 60°}{2} = 24°44' \qquad \frac{109°28' - 90°}{2} = +\ 9°44' \qquad \frac{109°28' - 108°}{2} = +\ 0.44°$$

You can conclude that as the size of ring increases, angle strain decreases. Hence, cyclopropane is most unstable compound, thus, most reactive.

Continued from Page 63

Correct Answers along with NCERT Text book Reference

1. **(b)** Page-42 Topic-Bohr's model for hydrogen atom.
2. **(a)** Page-42 Topic-Bohr's model for hydrogen atom
3. **(a)** Page-42 Topic-Bohr's model for hydrogen atom.
4. **(a)** Page-42 Table-2.3 The spectral line for atomic hydrogen.
5. **(c)** Page-42 Fig 2.11-Transition of the electron in the hydrogen atom.
6. **(d)** Page-43 Topic-Bohr's model for hydrogen atom. (postulates)
7. **(b)** Page-43 Topic-Bohr's model for hydrogen atom (postulates)
8. **(b)** Page-43 Box matter-Angular momentum.
9. **(b)** Page-43 Sub-topic-Postulates of Bohr's model [point-iv(a)]
10. **(a)** Page-43 Sub-topic-Postulates of Bohr's model [point-iv(b)]
11. **(d)** Page-43 Sub-topic-Postulates of Bohr's model [point-iv]
12. **(d)** Page-43 Sub-topic-Postulates of Bohr's model [point-iv]
13. **(a)** Page-43 Sub-topic-Postulates of Bohr's model [point-iv]
14. **(d)** Page-43 Topic-Postulates of Bohr's model for H-atom.
15. **(d)** Page 44 Box matter-What does the negative electronic energy for H-atom mean?
16. **(a)** Page-44 Sub topic-Postulates of Bohr's model for H-atom [point-iv-(c)]
17. **(c)** Page-44 Sub-topic-Postulates of Bohr's model for H-atom [point-iv (c)]
18. **(d)** Page-44 Sub-topic-Postulates of Bohr's model for H-atom [point-iv (d)]
19. **(a)** Page-44 Sub-topic-Postulates of Bohr's model for H-atom [point-iv (d)]
20. **(d)** Page-44 Sub-topic-Postulate of Bohr's mode for H-atom [point-iv (d), (e)]
21. **(a)** Page-44 Topic-Explanation of Line spectrum of hydrogen
22. **(d)** Page-45 Topic-Explanation of line spectrum of hydrogen
23. **(a)** Page-45 Topic-Explanation of line spectrum of hydrogen
24. **(a)** Page-45 Topic-Explanation of line spectrum of hydrogen
25. **(b)** Page-45 Topic-Explanation of line spectrum of hydrogen
26. **(a)** Page-45 Topic-Explanation of line spectrum of hydrogen
27. **(d)** Page-45 Topic-Explanation of line spectrum of hydrogen
28. **(d)** Page-45 Topic-Limitation of Bohr's model
29. **(a)** Page-45 Topic-Limitation of Bohr's model [point-i]
30. **(a)** Page-46 Topic-Limitation of Bohr's model [point-i]

CONCEPT MISCONCEPT

General Perception A viscous liquid is denser than non-viscous liquid.

Reality There is no relationship between the viscosity and density of a liquid.

Explanation A liquid viscosity is measured by its resistance to flow, while density is the amount of mass occupying per unit space or volume. e.g. oil is more viscous than water yet oil is less denser than water as it floats on water.

General Perception Nucleophilicity and basicity are the same terms.

Reality Basicity is a particular kind of nucleophilicity.

Explanation Nucleophilicity is a kinetic phenomenon while basicity is a thermodynamic phenomenon. Nucleophilicity is the relation between rate of the reactions of nucleophilies and a standard substrate in a standard solvent.

e.g. $CH_3I \xrightarrow[H_2O]{Nu^-} CH_3Nu + I^-$

Basicity is based on the position of equilibrium in a reaction of base with a proton donor species.

e.g. $\underset{\text{Base}}{B^-} + \underset{\text{Proton donar species}}{H_2SO_4} \rightleftharpoons \underset{\text{Conjugate acid}}{BH} + \underset{\text{Conjugate base}}{HSO_4^-}$

General Perception Concentration of pure solid and pure liquid is always unity.

Reality Concentration of pure solid or pure liquid is always constant.

Explanation As concentration $(C) = \frac{n \text{ (number of moles)}}{V \text{ (volume)}}$

$$= \frac{m}{M \times V};\ C = \frac{d}{M} \qquad \left(\because d = \frac{m}{V}\right)$$

Since, density (d) and molar mass (M) of pure solid or pure liquid is constant, therefore their concentrations are constant and not unity.

While solving emf of a cell, using Nernst equation, the concentration of pure solid or pure liquid is taken unity so that they do not appear in the net equation.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} \times \frac{[Cu]}{[Zn]}$$

$$= \underbrace{E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}}_{\text{I}} - \underbrace{\frac{0.0591}{n}\log\frac{[Cu]}{[Zn]}}_{\text{II}}$$

The term II has to be zero, since [Cu] and [Zn] are constants, It'll be zero only when [Cu] = [Zn] = 1

$\because \log_{10} 1 = 0$

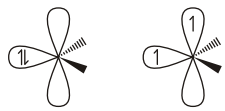
General Perception Reaction intermediate carbene, is an electrophile.

Reality Carbene acts as an electrophile as well as a nucleophile depending upon the reaction conditions.

Explanation A carbene is a molecule containing a neutral carbon atom with two unshared valence electrons. The general representation of carbene is :C<

Carbenes exist in two forms; singlet and triplet carbene.

Singlet carbene with empty p-orbital acts as an electrophile, while triplet carbene with a pair of unshared electrons act as a nucleophile.



General Perception Atomic radius decreases across a period, therefore noble gases have the smallest radii in their respective periods.

Reality Radius of noble gases is highest in their respective periods.

Explanation Radius of noble gases is only van der Waals' radius (as these are present in monoatomic form) and van der Waals' radius is always larger than the covalent radius. Hence, the radii of noble gases are highest in their respective periods.

General Perception In aqueous medium the increasing order of basicity of amines is

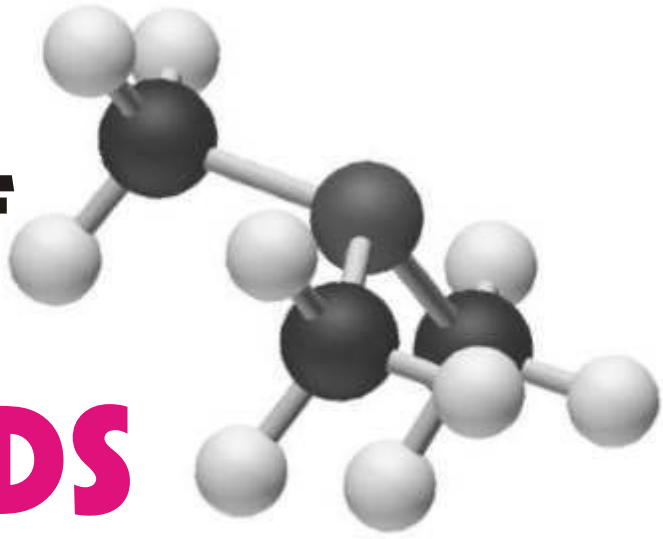
$$CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$$

This is due to increase in number of groups showing $+I$-effect.

Reality The increasing order of basicity of amines is

$$(CH_3)_3N < CH_3NH_2 > (CH_3)_2NH$$

Explanation In aqueous solution the basicity of amines depends upon several factors such as $+I$-effect, steric hindrance, solute–solvent linkage. On the basis of combined effect of these factors, the order of basicity of amines in aqueous solution is, $(CH_3)_3N < CH_3NH_2 > (CH_3)_2NH$.



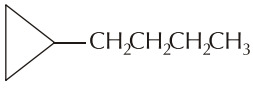
NOMENCLATURE OF ORGANIC COMPOUNDS PART 3

This section is targetted to provide an insight of IUPAC nomenclature of organic and inorganic compounds through questions as every year atleast 1-2 questions are asked on IUPAC nomenclature in all the competitive exams and boards.

Rules related to branch selection and numbering in cyclic and aromatic compounds

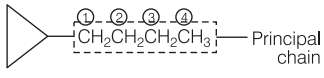
We have read about numbering of longest carbon chain in the last issue. Now, in this issue we shall read how to select branch and numbering in case of cyclic and aromatic compounds. Lets start with some examples.

Example 1

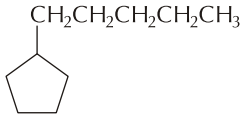


Sol. **Rule**

- *The ring is designated as a substituent, if the alkyl chain contains a greater number of C-atoms than the ring.*
- *Numbering will start from the carbon attached to the ring.*

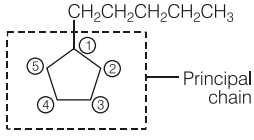


Example 2

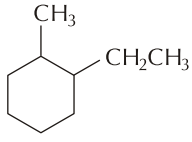


Sol. **Rule**

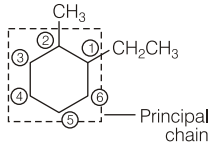
- *If the ring contains same number or greater number carbon atoms as that of alkyl chain, then ring is considered as principal chain.*
- *The numbering will start from the carbon attached to the alkyl chain.*



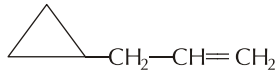
Example 3



Sol. **Rule** *While numbering the C-atoms of the ring, the substituent which comes first in alphabetical order is given the lowest number provided that it does not violate the lowest sum rule.*

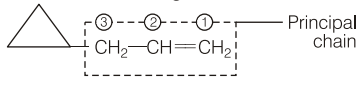


Example 4

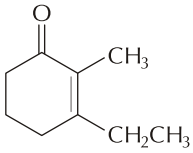


Sol. **Rule**

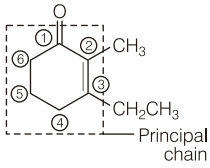
- *If the alkyl chain contains a multiple bond or a functional group, then the ring is treated as a substituent irrespective of the size of ring.*
- *The numbering is done by giving more preference to double bond rather than the ring.*



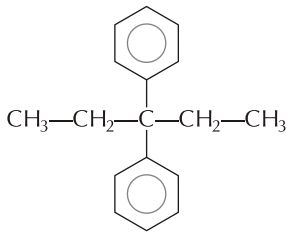
Example 5



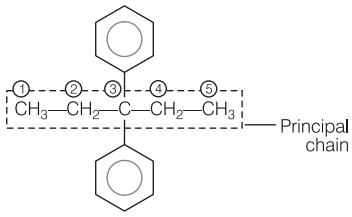
Sol. **Rule** *If some functional group alongwith substituent group(s) and multiple bond(s), is present in the ring, then numbering is done in such a way that the functional group gets the least possible number, among functional group, multiple bond(s) and substituent(s).*



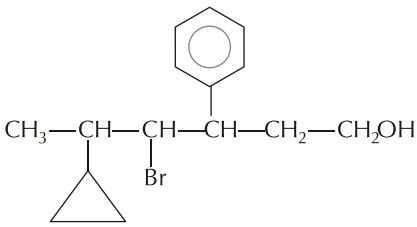
Example 6



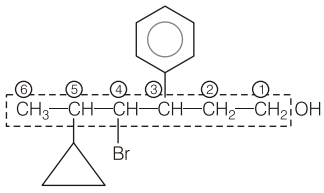
Sol. **Rule** *If the aromatic compound has an open chain attached to benzene, then this chain gets the main status; ring is treated as substituent.*



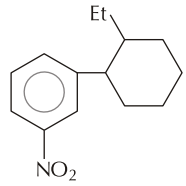
Example 7



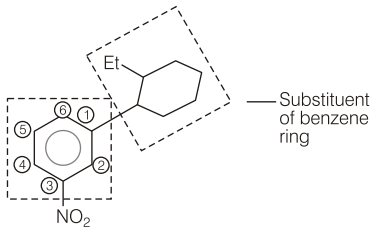
Sol. **Rule** *Numbering is done in such a way that functional group gets the lowest possible number.*



Example 8

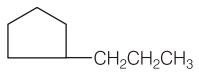
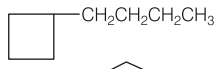
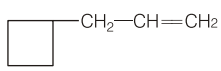
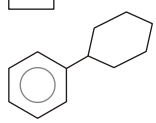
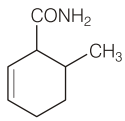
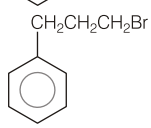


Sol. **Rule** *If a compound contains an alicyclic ring directly linked to the benzene ring, it is considered as derivative of benzene ring.*

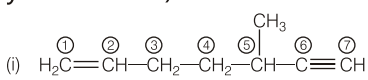


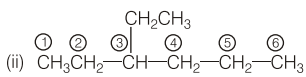
Practice Problems

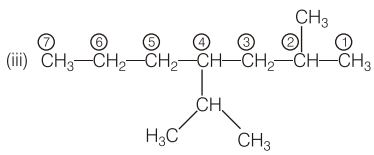
Select the longest possible chain in the following compounds and assign numbering as per the IUPAC rule.

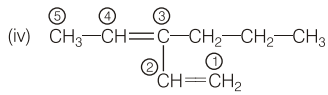
1. 
2. 
3. 
4. 
5. 
6. 

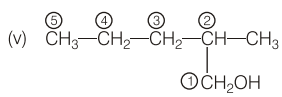
Practice Problems Answers
(July 2016 Issue)

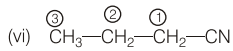
(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

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JUST SOLVE & SEND KNOWLEDGE COEFFICIENT QUIZZER (NO. 21)

1. In an experiment, copper sulphide reacts with nitric acid as

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 3S(s) + 4H_2O(g) + 2NO(g)$$

the volume of moist NO gas at 27°C and 1 atm pressure was collected in a chamber with 1642 mm × 760 mm × 30 mm in dimensions. Calculate the amount of copper sulphide taken and the volume of 8 M nitric acid required for the reaction. The vapour pressure of pure water at 27°C is 277 mm Hg.

(a) 44.04 g, 0.734 L *(b)* 88.08 g, 0.734 L
(c) 44.04 g, 0.367 L *(d)* 88.08 g, 0.367 L

2. Calculate the energy required to excite 1 L of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 $kJmol^{-1}$.

(a) 49.04 kJ *(b)* 38.49 kJ
(c) 87.12 kJ *(d)* 98.19 kJ

3. A sample of radium is emitted α-particles at an average rate of 2.24×10^{13} α-particles per minute. Each α-particle takes up two electrons from surroundings and form He-atom. During a period of 420 days, the volume of He gas was measured and was found to be 0.5 mL at 27°C and 750 mm of Hg. Using the given data calculate the value of Avogadro's constant.

(a) 6.023×10^{23}
(b) 6.784×10^{23}
(c) 6.171×10^{23}
(d) 6.001×10^{23}

4. A slice of banana weighing 2.502 g was burnt in a bomb calorimeter producing a temperature rise of 3.05°C. The combustion of 0.316 g of benzoic acid in the same calorimeter produced a temperature rise of 3.24°C. The heat of combustion of benzoic acid at constant volume is $-3227\ kJmol^{-1}$. If average banana weigh 125 g, how many calories can be obtained from one average banana?

(a) 46.98 kcal *(b)* 29.29 kcal
(c) 93.97 kcal *(d)* 80.43 kcal

5. Which of the following statement(s) is/are correct?

I. $CH_2 = CHOCH_3$ can be readily cleaved by dilute acids to a mixture of a carbonyl compound and an alcohol.

II. When acetophenone poured into H_3O^{18+} the recovered acetophenone contains O^{18}.

III. Oximes are more acidic than hydroxyl amines

Choose the correct option

(a) Only I *(b)* Only III
(c) II and III *(d)* All of these

6. A bubble of gas released at the bottom of a lake increases to eight times of its original volume when it reaches the surface. Assuming that atmospheric pressure is equivalent to the pressure exerted by a column of water of 10 m height, the depth of the lake is

(a) 80 m *(b)* 90 m *(c)* 40 m *(d)* 70 m

7. E°_{cell} for some half-cell reactions are given below. On the basis of these mark the correct answer.

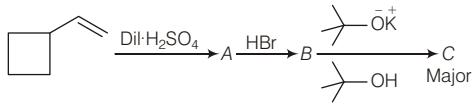
I. $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$, $E^\circ_{cell} = 0.00\ V$

II. $2H_2O^+(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$, $E^\circ_{cell} = 1.23\ V$

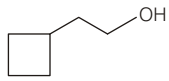
III. $2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$, $E^\circ_{cell} = 1.96\ V$

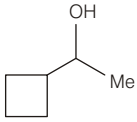
(a) In dilute sulphuric acid solution, hydrogen will be reduced at cathode
(b) In concentrated sulphuric acid solution, water will be oxidised at anode
(c) In dilute sulphuric acid solution, water will be oxidised at cathode
(d) In dilute sulphuric acid solution, SO_4^{2-} ion will be oxidised to tetrathionate ion at anode

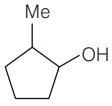
8. Consider the following reaction sequence

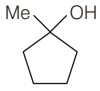


The structure of compound *C* is

(a) 

(b) 

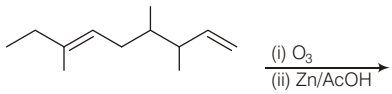
(c) 

(d) 

9. A solution of weak acid H*A* is being titrated with 0.01 M NaOH solution. End point is reached on addition of x mL of NaOH. To above solution, $\frac{x}{2}$ mL of 0.01 M HCl is added further pH of the resulting solution was found to be 5.3. Determine pH of the NaOH at end point if initial concentration of acid was 0.10 M.

(a) 7 *(b)* 8 *(c)* 9 *(d)* 6

10. How many optically active stereoisomers are possible by all the products formed during the ozonolysis of the following compound?



(a) 2 *(b)* 4 *(c)* 5 *(d)* 1

KNOWLEDGE Coefficient

Quizzer (No. 20)

Q. No.	a.	b.	c.	d.	Q. No.	a.	b.	c.	d.
1.	○	○	○	○	6.	○	○	○	○
2.	○	○	○	○	7.	○	○	○	○
3.	○	○	○	○	8.	○	○	○	○
4.	○	○	○	○	9.	○	○	○	○
5.	○	○	○	○	10.	○	○	○	○

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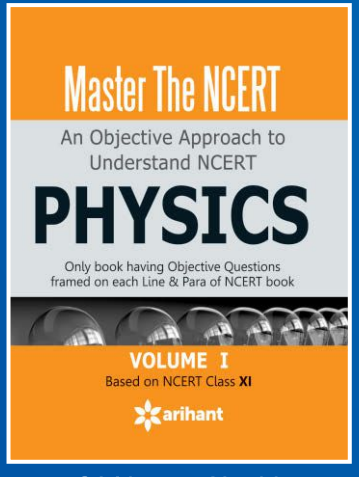
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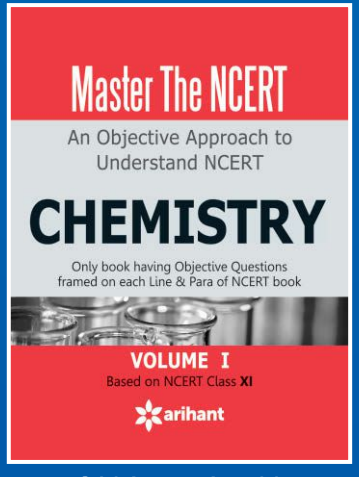
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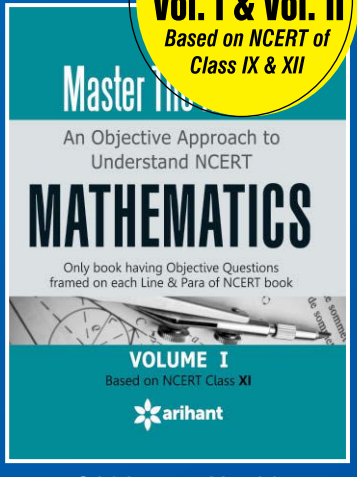
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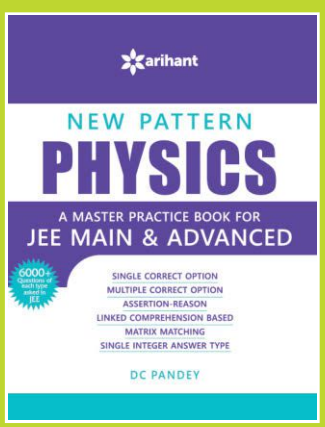

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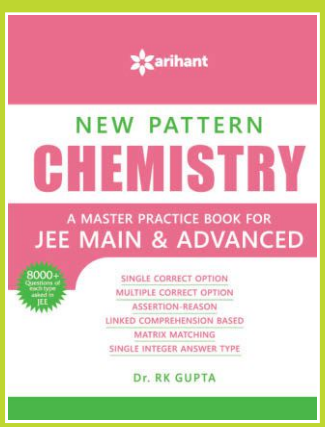

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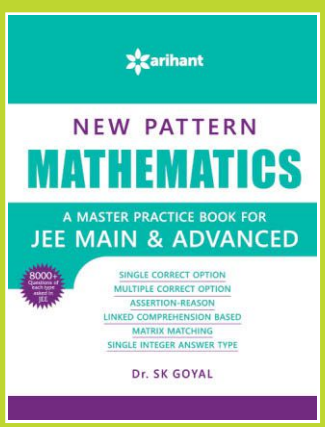

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